

# Kinetic simulation of methane combustion reaction: from mechanism to application

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*Abstract*—Based on the detailed mechanism model of the methane combustion, the kinetic parameters of the global reaction, such as pre-exponential factors and activation energy, are modeled and solved. The variations of concentration of the radicals and components over time are shown for certain mechanism models, and that for global models as well. The algebraic relationship deduced from elementary reactions to global reactions are also discussed. By the method proposed, the dynamic parameters of the global reaction from essential mechanism model were drawn and compared with those from literature. Correspondingly, this paper proposed an approach to achieve the kinetic parameters of certain global reaction, in application, from available mechanism models.

*Keywords* — reaction mechanism, global reaction, reaction rate constant, pre-exponential factor, activation energy

## I. INTRODUCTION

Since the first industrial revolution, global energy consumption has been dominated by primary energy, among which fossil fuel consumption is the largest. Natural gas is an important fossil fuel with large global reserves. In recent years, the use of natural gas has gradually increased. In 2017, global natural gas consumption increased by 96 billion cubic meters<sup>[1]</sup>, up by 3%, which is the fastest growth rate since 2010. Methane is the main component of natural gas, and the most common use is the combustion of methane. Currently, methane combustion mechanisms include GRI-Mech3.0<sup>[2]</sup>, Konnov mechanism<sup>[3]</sup>, Leads mechanism<sup>[4]</sup>, Williams mechanism<sup>[5]</sup>, etc. The GRI-Mech3.0 given by the university of California, Berkeley is the most detailed. The detailed combustion mechanism of methane is complex, and there are many intermediate products in the reaction process. It will take more time in numerical simulation.

The methane combustion reaction mechanism used in this paper is GRI-Mech3.0. Numerical simulation is carried out by COMSOL Multiphysics. The data obtained are used to solve the kinetic parameters of the simplified mechanism of the total package reaction, such as pre-exponential factor and activation energy, etc.

## II. PRINCIPLE

### A. Reaction kinetics

Chemical reaction kinetics studies the rate and reaction mechanism of chemical reactions, as well as the influence of external factors such as temperature and pressure on the reaction rate<sup>[6,7]</sup>. Elementary reaction usually refers to the chemical reaction that can be completed in one step. The so-called one-step reaction is that molecules, atoms, free radicals and so on can be transformed into products after one collision. The most basic unit of chemical kinetics is the elementary reaction.

The reaction rate of primitive reaction can be solved by using the law of mass action, which expresses the relationship between the reaction rate and the concentration of reactants.

For elementary reaction



The law of mass action is

$$r = k[A]^{na}[B]^{nb} \quad (2)$$

where  $k$  is the rate constant, the physical meaning of which is the reaction rate when all reactants are of unit concentration.  $[A]$  and  $[B]$  represent the concentrations of reactants  $A$  and  $B$  respectively.  $na$  and  $nb$  are the order of reactants  $a$  and  $b$  in this reaction. The law of mass action only applies to elementary reactions.

The law of mass action commonly used is in differential form, also known as rate equation, which mainly represents the relationship between reaction rate and concentration of chemical reaction, namely

$$r_A = -dc_A/dt \quad (3)$$

the integral form of the law of action of mass can be obtained by integrating (3), which can be used to express the relationship between the concentration and time and other parameters, also known as the dynamic equation.

A change in temperature will have a drastic effect on the reaction rate. Van't Hoff put forward the rule that the reaction rate increases approximately by 2~4 times for every 10K

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increase in temperature. In 1889, Arrhenius put forward the Arrhenius formula on the basis of van't Hoff's approximation law, and pointed out the direct relationship between reaction rate constant  $k$  and temperature, preexponential factor and activation energy. The form is as follows:

$$k = A e^{-Ea/RT} \quad (4)$$

where  $A$  is the preexponential factor and  $Ea$  is the activation energy, both of which are independent of temperature.  $R$  is the molar gas constant, whose value is  $8.314 \text{ J}/(\text{mol} \cdot \text{K})$ , and  $T$  is the temperature.

It can be seen that the reaction rate coefficient  $k$  will change with the change of temperature, which reflects the influence of temperature on the reaction rate.

### B. Scheme

Global reaction is a collection of elementary reactions, which represents a stoichiometric expression of the total results of elementary reactions. The main purpose of this paper is to solve the kinetic parameters of global reaction.

The solution of order of reaction and rate constant mainly uses differential method, that is, the logarithmic form of reaction rate equation

$$\ln(-dc_A/dt) = \ln k_A + n_A \ln c_A + n_B \ln c_B \quad (5)$$

when the concentration of B is constant, can get

$$\ln(-dc_A/dt) = \ln k + n_A \ln c_A \quad (6)$$

At this time, the order of the substance A needs to be known only by knowing the change of the concentration of the substance A with time. After solving, we can get a curve about  $\ln(-dc_A/dt)$  and  $\ln c_A$ . The curve is then linearly fitted to obtain the slope of the line as the reaction order of the substance A, the intercept is related to the rate constant  $k$  and the concentration of the substance B. By using the same method to keep the concentration of substance A constant, the number of stages of substance B can be obtained, and the reaction rate constant  $k$  at this temperature can be solved.

The solution of pre-exponential factor and activation energy is to use the logarithmic form of Arrhenius formula on the basis of obtaining reaction rate constant  $k$  at different temperatures

$$\ln k = -Ea/RT + \ln A \quad (7)$$

By substituting the rate constants  $k$  at different temperatures into equation (7), the curves related to  $\ln k$  and  $1/T$  can be obtained. The curve is fitted linearly, and the slope of the line is  $-Ea/R$ , and the intercept is the logarithm of the pre-exponential factor  $A$  based on the natural index.

## III. MODELING

The mechanism of methane combustion Gri-Mech3.0, by the university of California, Berkeley, contains 53 substances and 325 elementary reactions in total. It can accurately simulate the change of substance concentration and temperature and pressure during methane combustion in the range of temperature from 1000 to 2500K and pressure from 10Torr to 10atm [2]. In this paper, methane combustion was simulated in COMSOL Multiphysics on this basis, so as to obtain the changes of physical quantities, such as

concentration and temperature, with time in the methane combustion reaction process.

The initial concentration of reactants was set as shown in Table I, and the initial temperature, pressure and external heating conditions of the reactor were set.

TABLE I. INITIAL CONCENTRATION OF REACTANT

	Reactant	
	O <sub>2</sub>	CH <sub>4</sub>
initial concentration $c_i(\text{mol}/\text{m}^3)$	20	10

The following is the numerical simulation of the concentration and temperature of the reactor at 1100 K, 10000 Pa and 0 external heating. The initial concentration of the reactant is consistent with that in Table I.

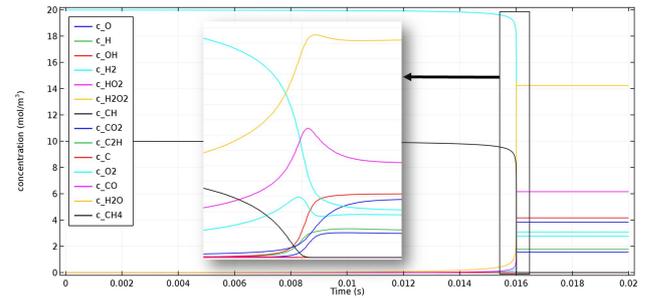


Fig. 1. The concentration change

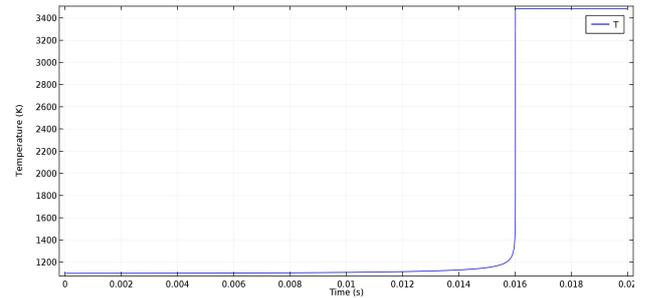


Fig. 2. The temperature change

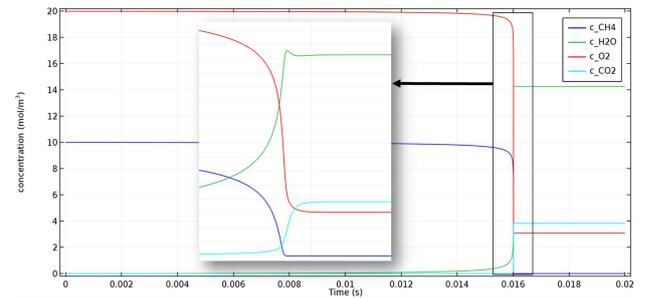
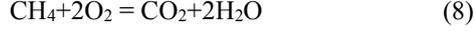


Fig. 3. Change in CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O concentration

The simulation above shows the reaction of methane in an adiabatic reactor. When the temperature in the reactor is kept unchanged, that is, the heat release of the reaction in the reactor is set equal to the heat loss of the reactor, the change curve of the concentration of reactants with time at a certain temperature can be obtained, and the data obtained at this time is the initial data used for the solution in this paper.

#### IV. RESULTS AND DISCUSSION

For a one-step global reaction, the reaction equation can be written as

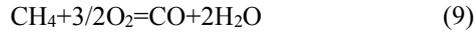


By using the calculation principle in II.B, the order of reactants of the global reaction and the reaction rate at different temperatures can be solved. And then the pre-exponential factor and activation energy of the reaction can be solved

TABLE II. KINETIC PARAMETERS OF ONE-STEP GLOBAL REACTION

$A(\text{mol}/\text{m}^3\cdot\text{s})$	$Ea(\text{J}/\text{mol})$	Order	
		$\text{O}_2$	$\text{CH}_4$
$9.9 \times 10^8$	185476	1.13	1.73

For the two-step global reaction mechanism, the reaction equation can be written as



By the same method, the pre-exponential factors, activation energy and reactant order of each reaction can be obtained

TABLE III. KINETIC PARAMETERS OF ONE-STEP GLOBAL REACTION

(9) <sup>a</sup>		Order	
$A(\text{mol}/\text{m}^3\cdot\text{s})$	$Ea(\text{J}/\text{mol})$	$\text{O}_2$	$\text{CH}_4$
$2.8 \times 10^8$	174925	1.79	1.19

<sup>a</sup> The first step in the two-step mechanism.

(10) <sup>b</sup>		Order	
$A(\text{mol}/\text{m}^3\cdot\text{s})$	$Ea(\text{J}/\text{mol})$	$\text{O}_2$	$\text{CO}$
$1.4 \times 10^8$	206201	0.88	1.76

<sup>b</sup> The second step in the two-step mechanism

In the actual combustion of methane, there is  $\text{H}_2\text{O}$  in the product.  $\text{H}_2\text{O}$  will have a certain influence on the second step reaction in the two-step reaction mechanism. Considering the influence of  $\text{H}_2\text{O}$  on the reaction, the order of  $\text{O}_2$  is 1.37, the order of  $\text{CO}$  is 1.52, and the order of  $\text{H}_2\text{O}$  is 1.15. In this case, the kinetic parameters are:  $A=9267.6 \text{ mol}/\text{m}^3\cdot\text{s}$ ,  $Ea=71464.9\text{J}/\text{mol}$ .

##### A. One-step global reaction

The one-step global mechanism model of methane combustion was established in COMSOL Multiphysics. The kinetic parameters in Table II were substituted into the model, and the reaction rate was defined as:

$$k_{\text{ONE}} * c_{\text{CH}_4}^{1.12} * c_{\text{O}_2}^{1.73} \quad (11)$$

The reactor parameters were set as an intermittent constant volume reactor, including energy balance, external heating or cooling capacity of 0, reactor pressure of 1atm, and reactor volume of  $1\text{m}^3$ . The initial temperature of the reaction was set at 1100K, the concentration of methane was  $10\text{mol}/\text{m}^3$ , and the concentration of oxygen was  $20\text{mol}/\text{m}^3$ .

The simulated changes of substance concentration and reactor temperature in the combustion process are as follows

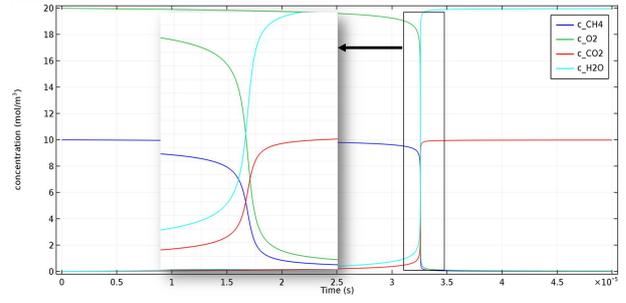


Fig. 4. The concentration change

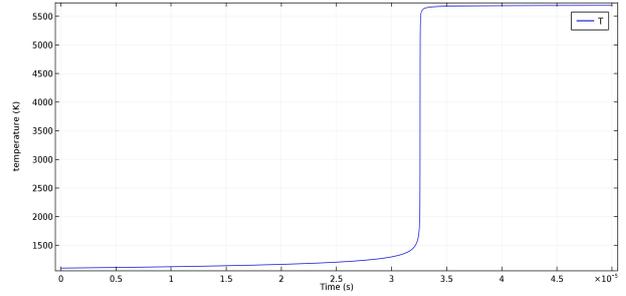


Fig. 5. The temperature change

As can be seen from the changes of substance concentration and temperature in the figure, the reaction was completed when the time reached  $0.5 \times 10^{-4}\text{s}$ . Compared with the detailed mechanism of methane combustion, the reaction time was shorter. Moreover, the reaction temperature can reach about 5700K after the one-step global mechanism is completed, and the temperature rise is about 4600K. Compared with the detailed mechanism, the temperature rise is relatively high, which cannot well simulate the temperature change in the methane combustion process. From here we see that there is a certain difference between the one-step global mechanism and detailed mechanism of methane combustion. Therefore, the one-step global mechanism is mostly used for qualitative analysis of combustion process, rather than quantitative analysis.

##### B. Two-step global reaction

The same as in the previous section, the two-step total package mechanism model of methane combustion is established by using the data in Table III. The difference lies in that the reaction rate of the model is defined as follows:

$$k_{\text{TWO}_1} * c_{\text{CH}_4}^{1.19} * c_{\text{O}_2}^{1.79} \quad (12)$$

$$k_{\text{TWO}_2} * c_{\text{CO}}^{1.76} * c_{\text{O}_2}^{0.88} \quad (13)$$

The reactor setting is the same as that in the previous section. The simulated changes in the concentration of substances in the combustion process and the reactor temperature are as follows:

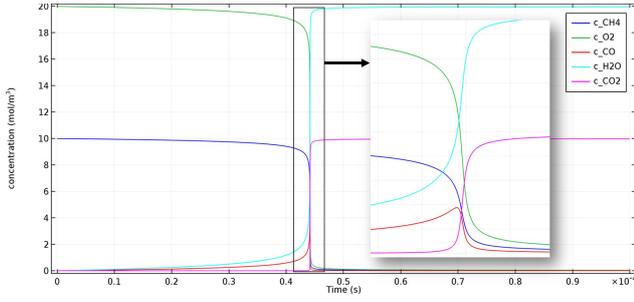


Fig. 6. The concentration change in global reaction

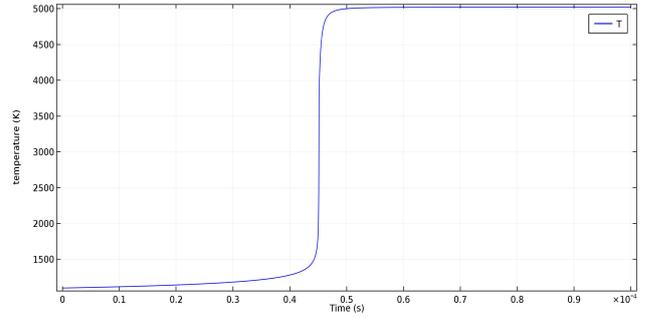


Fig. 9. The temperature change (Including H2O)

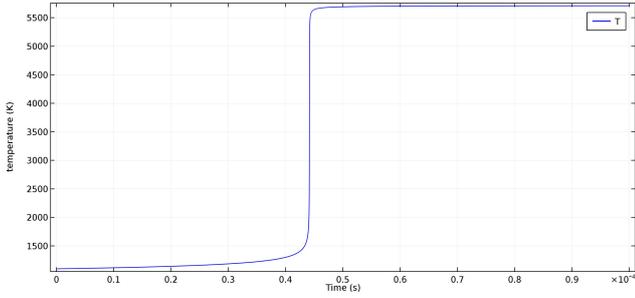


Fig. 7. The temperature change in global reaction

As can be seen from Fig.6, the reaction was basically completed before  $5 \times 10^{-5}$ s, and CO would appear in the reaction, which is close to the actual combustion situation of methane. As can be seen from Fig.7, the final combustion temperature of the two-step global mechanism of methane is about 5000K, and the temperature rise is about 3900K, which is also deviated from the actual combustion of methane. Thus it can be seen that the two-step global mechanism can well simulate the change of CO concentration in the methane combustion process, but there is a certain deviation in the simulation of other substance concentration changes and temperature changes.

The above results are obtained when the two-step global mechanism does not consider the influence of water. When the influence of water is taken into account in the second step of the two-step global mechanism, the reaction rate of the second step should be defined as

$$k_{TWO\_2} * c_{CO}^{1.52} * c_{O_2}^{1.37} * c_{H_2O}^{1.15} \quad (14)$$

The change curve of temperature and substance concentration can be obtained as follows:

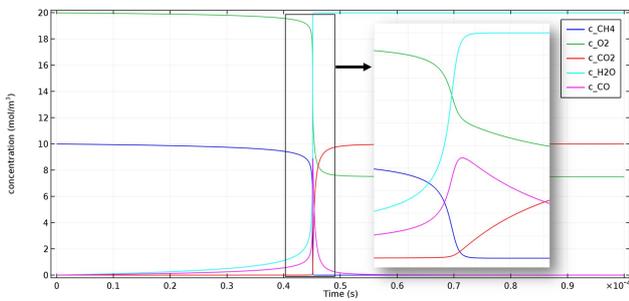


Fig. 8 The concentration change (Including H2O)

The concentration change in the two-step global reaction considering H<sub>2</sub>O is slightly slower than that in the two-step global reaction without H<sub>2</sub>O. The final temperature of both of them is the same, which is about 5000K.

### C. Comparison for one-step global mechanism

In this section, the kinetic parameters of the one-step global mechanism obtained in this paper and the results of previous researchers<sup>[8,9,10,11,12]</sup> were used to establish methane combustion models in COMSOL Multiphysics respectively, and to compare these models.

When the model was established, the reaction rate was selected as user-defined, that is, it changed with the change of order of different global mechanism. The parameters of the reactor were set as in the previous section: the pressure was 1atm, and the volume was 1m<sup>3</sup>. The initial temperature of the reaction was set at 1100K, the concentration of methane was 10mol/m<sup>3</sup>, and the concentration of oxygen was 20mol/m<sup>3</sup>. After the simulation, the one-step global combustion mechanism concentration changes (taking methane as an example) and temperature changes in different situations can be obtained, which are summarized as follows:

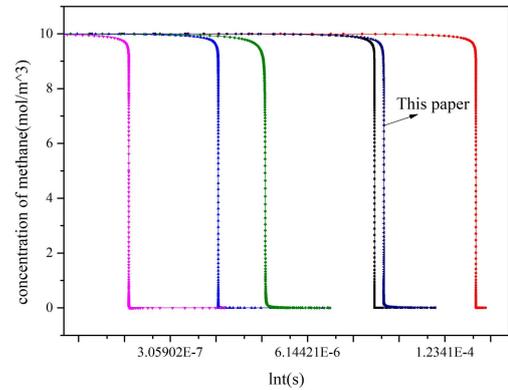


Fig. 10. The concentration change(taking methane as an example)

The rate of reactant consumption of the one-step global mechanism of methane combustion calculated in this paper is close to that of the global mechanism in literature, and the reaction completion time is in good agreement. And all the methane burners have the same temperature rise.

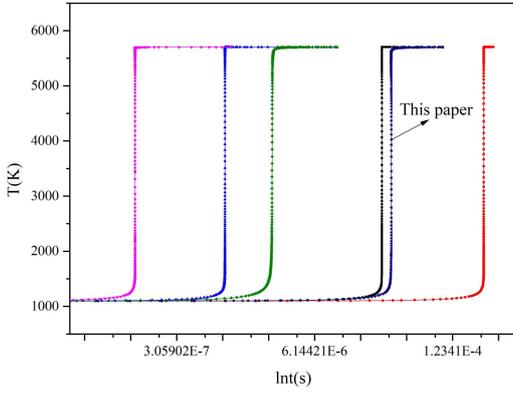


Fig. 11. The temperature change

#### D. Comparison of different mechanisms

In this section, the one-step and two-step methane combustion mechanisms obtained in this paper are compared with the detailed methane combustion mechanism to analyze their reliability and applicability. The following also takes the methane concentration change as an example to draw the methane concentration change curve and temperature change curve of different mechanisms under the same reaction condition.

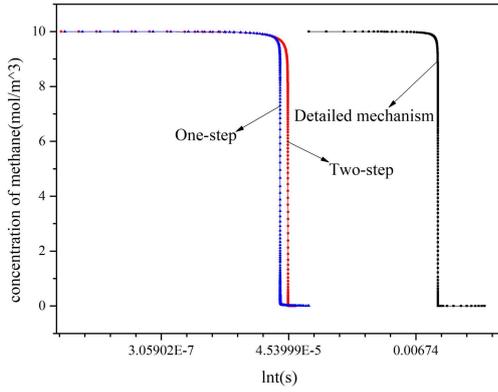


Fig. 12. Concentration changes of different mechanisms(taking methane as an example)

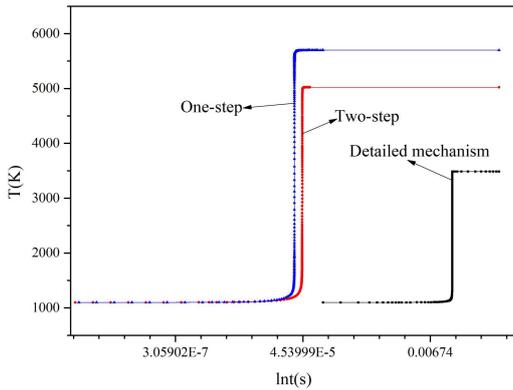


Fig. 13. Temperature variations in different mechanisms

In order to facilitate the observation of the relationship between different mechanisms, the abscissa of Fig.12 and Fig.13 adopts the logarithmic coordinate axis.

As can be seen from the figure, the reaction rate of the global combustion mechanism of methane is much faster than that of the detailed combustion mechanism, and the methane consumption in the global combustion mechanism starts earlier, which is caused by the fact that there are fewer intermediate products in the reaction process of the global combustion mechanism and the reaction process is relatively simple. At the same time, the combustion temperature of the one-step and two-step global mechanism is quite different from the actual situation.

#### E. Discussion on Temperature Rise

In this paper, the constant volume adiabatic combustion model is adopted, so the energy conservation and reaction enthalpy in the reaction process can be used to solve the final temperature  $T_{ad}$  of the reaction process

$$H_{\text{reac}} - H_{\text{prod}} - R_u(N_{\text{reac}}T_{\text{init}} - N_{\text{prod}}T_{\text{ad}}) = 0 \quad (15)$$

where  $H_{\text{prod}}$  and  $H_{\text{reac}}$  are enthalpy of products and reactants respectively,  $N_{\text{reac}}$  and  $N_{\text{prod}}$  are the stoichiometric Numbers for the reactants and the products,  $T_{\text{init}}$  is the initial temperature.

It is found from the previous content of this paper that under the initial reaction temperature of 1100K, the final adiabatic reaction temperature of different mechanisms is not the same. The final reaction temperature of the detailed mechanism is about 3500K, and the temperature rises to 2400K. The final reaction temperature of the global reaction mechanism is about 5700K, and the temperature rise is 4700K.

From the detailed mechanism to the global mechanism, under the same reactant concentration and the same reactor parameters, the temperature rise of the reaction process increases gradually. It can be known from (15) that the temperature rise of the reaction process is related to the reaction enthalpy. From the detailed mechanism to the global mechanism, there are fewer and fewer substances in the reaction process. In the actual situation that the intermediate of the reaction cannot be completely consumed, the amount of the final product of the reaction is also less and less. The final products of the detailed mechanism are  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}$ ,  $\text{OH}$ ,  $\text{CH}_3$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_2$ , etc. The final products of the global mechanism are  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Since the initial state set by different reaction mechanism models is the same, that is, the total enthalpy of reactants is the same. However, the number and types of products of different reaction mechanisms are not the same, and the absolute enthalpy of different substances is different, that is, the total enthalpy of products of different reaction mechanisms is different. The total enthalpy of the reactants is the same, and the total enthalpy of the products is different, that is, the reaction enthalpy is different in the reaction process. And we know from (15) that this is going to change the temperature at which the reaction ends. Therefore, the temperature rise of different reaction mechanisms is different, which is caused by the different types and quantities of products in the reaction process.

#### V. CONCLUSIONS

In this paper, the kinetic parameters of the global combustion mechanism of methane are obtained by solving the variation of the concentration of substances during the

combustion of methane based on the knowledge of reaction kinetics. The temperature rise in different reaction processes of methane combustion is also discussed. The main conclusions are as follows:

1) A model of different methane combustion mechanisms was established in COMSOL Multiphysics. By simulating the change of material concentration with time in the combustion process, the correlation between reaction rates of different reaction mechanisms could be obtained. The temperature rise of different reaction mechanism can be obtained from the temperature change during combustion. Comparing different reaction mechanisms, it can be found that at the same initial temperature, the temperature rise of detailed mechanism of methane combustion is the lowest, and the temperature rise of global mechanism is higher than that of detailed mechanism. Under the same conditions, the reaction delay time of detailed mechanism of methane combustion is the longest, and the simpler the model is, the shorter the corresponding reaction delay time will be.

2) The concentration of substances at different times can be obtained from the detailed mechanism of methane combustion. By using these data and combining with the reaction rate equation and Arrhenius formula in the reaction kinetics, the order of substances and kinetic parameters in the total reaction mechanism can be solved. For the one-step global reaction, the parameters solved in this paper are shown in Table II, and the kinetic parameters of the two-step global reaction are shown in Table III. In this paper, the one-step global reaction mechanism is close to the one step global reaction mechanism in the literature, but it is different from the detailed combustion mechanism. The reaction end time of the two-step global reaction mechanism is also much earlier than the detailed methane combustion mechanism, so the global methane combustion mechanism can only be used for qualitative analysis of the methane combustion process, but not for quantitative analysis.

3) After establishing different methane combustion models, it was found that under the same initial conditions,

the reaction temperatures of different methane combustion mechanisms were different. It was found that the final temperature of different reaction mechanisms was different, which was caused by different types and quantities of products in different mechanisms

#### ACKNOWLEDGMENT

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