



THE CH₄ COMBUSTION MODEL

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Abstract

This paper presents the research effect of the modeling of the CH₄ combustion process in different conditions. Presented model was prepared with using the GriMech 3 chemical kinetic mechanism of methane combustion. Its mechanism developed by research unit from University of Berkley and verified by more than 140 science publications. Mechanism GriMech 3 consist of description of reactions between 52 assumed chemical species and thermodynamic data of these reactions and chemical species. The paper presents algorithm of calculations the summarize heat release from combustion process and changing of chemical species mole fractions. Calculations was prepared for different temperature from 1100K to 3600K, different pressure from 2MPa to 5MPa and different combusted mixture composition (changing the humidity of air from 4,5 to 30g_{H2O}/kg of air and air-fuel excess ratio from 0.8 to 2.5). Obtained results of calculations show dependences between mentioned parameters and time of combustion process. Increase temperature and/or pressure of combustion accelerate the combustion process and same process stay sudden. Increasing the quantity of air in fuel mixture causes a significant drop of the maximum heat release but accelerates the combustion process. The changing of quantity of water in combusted mixture not give the significant effect in heat release but changes mole fractions of a few chemical species.

Keywords: combustion process, model, combustion engines, methane, kinetic calculation, GriMech 3

1. Introduction

Most popular source of energy in the world transportation is a combustion process of many kinds' hydrocarbon fuels in different constructions of internal combustion engines [1]. Energy machines, uses this kind of process, are still no effective constructions, emitted into the atmosphere a lot of kinds of toxic gaseous compounds. [2]. For this reason, the intensive research on improving the efficiency of combustion and conversion energy processes carried out. Mathematical models are commonly used to designing and testing the processes of combustion of hydrocarbon fuels [3]. Most popular and effective methods of combustion processes calculation are methods based on finite element methods. They rely on dividing the combustion chamber on smaller elements, in which the phenomenon of mixing and the fuel combustion and the mass and energy exchange with the environment are mathematical described [4]. Finite element methods, however, require substantial computing power due to the complexity of phenomena occurring in the combustion chambers of energy machines. The example of this situation is work of the diesel engine [5]. During the compression process of air in the combustion chamber of the engine, the liquid fuel injection process occurs. During compression of air and fuel injection simultaneously take place the following phenomena: the atomization and the vaporization of liquid hydrocarbon fuel, its turbulent mixing in air, the self-ignition and the combustion process according to complex

chemical reactions of fuel oxidation. Parameters of mentioned phenomena depend on local concentrations of chemical components of the combusted mixture and local thermodynamic parameters [6]. Due to the motion of the piston, the fuel injection into the combustion chamber and the course of various phenomena of the combustion process takes place in dynamic and heterogeneous conditions in different areas of the engine cylinder. For these reasons, the accuracy of the combustion process modeling also depends on the chosen quantity and the size for finite elements and the accuracy of the description of phenomena occurring in elements. Constantly increasing computational power of computers, however, is still too small for a comprehensive modeling of combustion in the combustion chamber with the use of methods based on Reynolds equations [7]. Therefore, used mathematical models are largely simplified, depending on the purpose of modeling [8]. In the case of models aimed at increasing the efficiency of the combustion processes commonly used simplification is the limitations of the mathematical description of the kinetic combustion process. Such a description is often introduced to a few chemical reactions in each finite element. For modeling the combustion process to reduce emissions of harmful and toxic substances in exhaust gases often used simplification is reduction of the finite elements number or simplified mathematical description of phenomena of heat transfer, mixing of fuel, etc. Each simplification, however, is a compromise between quality and cost modeling.

As a result of the kinetic modeling of the combustion process achieved a continuous function of energy from the fuel dose combustion, depending on mole concentrations of individual chemical species of the combustible mixture, temperature, pressure and time of the combustion. The values of such functions in the combustion process modeling should be carried out for a considered time to determine the energy balances of individual finite elements [9]. The resulting energy function can then be used to model the instantaneous energy states of individual finite elements in various types of combustion chambers of engines.

The paper presents the kinetic model of hydrocarbon fuel combustion in air on the example of methane under conditions of variable pressure and variable temperature. The calculation results are presented for different molar concentrations of fuel and oxidizer and variable humidity of air.

2. The combustion process model

Commonly used hydrocarbon fuels are usually delivered to customers in liquid form, as a mixture of many, often complex, hydrocarbon compounds. The variety compositions of various hydrocarbon fuels make the designation of the composition strictly impossible in practice. It should also be noted that the fuel processing, the storage and transportation conditions contribute to changes in the chemical composition of delivered fuel. On the other hand, fuel supplied to the energy machine before combustion is usually prepared. In the case of internal combustion engines, fuel supplied to the combustion chamber is atomized and evaporated (in the case of liquid fuels) and in the next stage combusted. The reason of this situation is necessity of the neighborhood of fuel and oxidizer particle, capable of initiating the ignition process. In parallel with these phenomena is the mixing of fuel with the oxidant (usually air) and the process of the thermal dissociation, causing the breaking of complex hydrocarbon chains of the simpler compounds. [10]. And so the combustion process is hydrocarbon fuel in gaseous form and the fuel composition is significantly different from the delivered to the engine.

In the modeling of combustion processes, therefore, the replacement composition of fuel are assumed, selected on the basis of the different criteria. Usually it's a molar ratio of carbon and hydrogen, similar to the average value of the unprepared fuel or the similar molar mass, the flash point, the heat release, etc. After the assumption of the replacement fuel composition the next stage of modeling is building a kinetic model of the combustion process. This model is built from partial chemical reactions based on their properties such as the required activation energy, molar

concentrations of substrates and products and the heat released or collected from the environment. These parameters change with the prevailing thermodynamic conditions and the presence of catalysts, and therefore the process of selecting the model of chemical reactions is usually tedious and proceeded by the theoretical and the experimental research. For that reason, we know only a few reliable and validated kinetic models of the hydrocarbon fuel combustion process [11].

The GriMech 3 kinetic mechanism was assumed to modeling the combustion process [12]. Assumed mechanism was developed by the research unit from University of Berkley and was optimized for natural gas combustion process. GriMech 3 mechanism was chose for reason of its simplicity and verifies at least 143 scientific publications [13]. The chosen model includes a description of the chemical reactions between 52 chemical species, the coefficients needed to determine the course of each reaction and thermodynamic data of considered chemical species. These data allow determining the molar concentrations of substrates, products, and heat release in various chemical reactions for selected thermodynamic parameters (temperature, pressure, composition of the mixture).

The first step of the calculation is defining the constant rate for all considered chemical reactions in the combustion process according to GriMech 3 mechanism. It was calculated with using Arrhenius equation:

$$k_i' = A \cdot T^\beta \cdot \exp(-E/RT), \quad (1)$$

where:

A and β - constant coefficients,

E - the activation energy,

R – the universal gas constant,

T – temperature.

and constant rate for reverse reaction:

$$k_i'' = \frac{k_i'}{K_{ci}}, \quad (2)$$

where:

K_{ci} – the equilibrium constant for the i -th reaction, determined by the following equation [14]:

$$K_{ci} = \left(\frac{p}{R \cdot T} \right)^{\sum_{k=1}^K (v_{ki}' - v_{ki}'')} \exp \left(\sum_{k=1}^K (v_{ki}' - v_{ki}'') \frac{S_k^0}{R} - \sum_{k=1}^K (v_{ki}' - v_{ki}'') \frac{H_k^0}{R \cdot T} \right), \quad (3)$$

where:

p - pressure,

S_k^0 – the standard state molar entropy of the k -th species,

H_k^0 – the standard state molar enthalpy of the k -th species,

v_{ki}' – the stoichiometric coefficient of k -th reactant species in the i -th reaction,

v_{ki}'' – the stoichiometric coefficients of k -th product species in the i -th reaction.

Obtained results allowed calculating rates of molar concentration change of chemical species by the following equation:

$$q_i = \left(\sum_{k=1}^K ((a_{ki}) \cdot [X_k]) \right) \cdot \left(k_{fi} \prod_{k=1}^K [X_k]^{v'_{ki}} - k_{ri} \prod_{k=1}^K [X_k]^{v''_{ki}} \right), \quad (4)$$

where:

a_{ki} – the enhanced third-body efficiency of the k -th species in the i -th reaction,
 X_k – the molar concentration of the k -th species.

Determination of the rate of change of the molar concentration for each chemical reaction highlighted the sum of molar concentrations of all chemical species for a given moment of time.

Based on Hess's law it's possible to designate the heat release from the chemical reaction mechanism. Assuming isothermal-isobaric combustion we can write for all considered reactions:

$$Q = \sum_{i=1}^I \left[\sum_{k=1}^K v_{ki}'' [H_k^T - H_k^0 + \Delta H_{fk}] - \sum_{k=1}^K v_{ki}' [H_k^T - H_k^0 + \Delta H_{fk}] \right], \quad (5)$$

where:

Q – the heat release from all considered reactions,
 H_k^T – the molar enthalpy of the k -th species at temperature T ,
 ΔH_{fk} – the enthalpy of formation k -th species.

The calculations are made using a spreadsheet for the data presented in Table 1.

Tab. 1. Parameters used to kinetic calculations according to GriMech 3 mechanism

Parameter	Value	Unit
Pressure p	2, 3, 4, 5	MPa
Temperature T	1100, 1600, 2100, 2600, 3100, 3600	K
Air humidity X	4,5; 10; 20; 30	g _{H2O} /kg of air
Air-fuel excess ratio λ	0,8; 1; 2,5	–
Time interval t	$1,5 \times 10^{-5}$	s

Combustion process parameters presented in Table 1 correspond to temperature and pressure in the combustion chamber of the marine diesel engine. Chosen air humidity correspond the engine charge air humidity from 20% at 20°C to 95% at 30°C and time interval corresponds to the rotation of the engine crankshaft by 0.1 degree at the engine working with 100 rpm. The calculations were made for the excess and deficiency of air to burn the fuel dose in the cylinder and quantity of charge enough (air-fuel excess ratio equal 1). Such conditions may arise in different areas of the engine combustion chamber.

The sequence of calculations was as follows: for selected parameters from Table 1, initial molar concentrations and mole fractions of chemical species were calculated. For selected temperature and pressure the forward and reverse constant rates of all reactions were calculated. Using these parameters the molar concentrations of chemical species after the time equal $1,5 \times 10^{-5}$ second were calculated by summation of molar concentrations of all reaction products. The total heat release from the combustion process was the sum of energy of each reaction [10], [14]. Obtained results were the input to the next stage of the calculation after an identical period of time, so that calculation results for different initial concentrations of combustion mixture were obtained.

Moreover, such an approach allows for the automation of calculations. In one series of calculations 1500 successive calculations were performed. The calculations are made for all possible configuration parameters set out in Table 1 (288 series of calculations for 1500 in one series).

Using the presented algorithm 432 thousands data sets were collected. All obtained data sets consists of 52 input mole fractions of chemical species, temperature and pressure, 52 output mole fractions of chemical species and the heat release from all considered reactions.

3. Results of calculation

Figure 1 shows example calculation results for chosen chemical species and thermodynamic parameters equal 1100K i 4MPa, 10g_{H2O}/kg humidity of air and air-fuel excess ratio equal 2,5. The quantity of chemical species is represented in mole fractions in the combustion mixture.

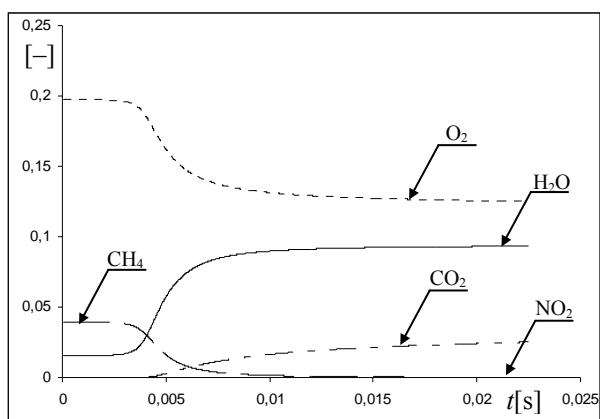


Fig. 1. Calculation results of mole fractions of chosen chemical species for $T=1100K$, $p=4MPa$, $X=10g_{H_2O}/kg$ of air and $\lambda=2,5$

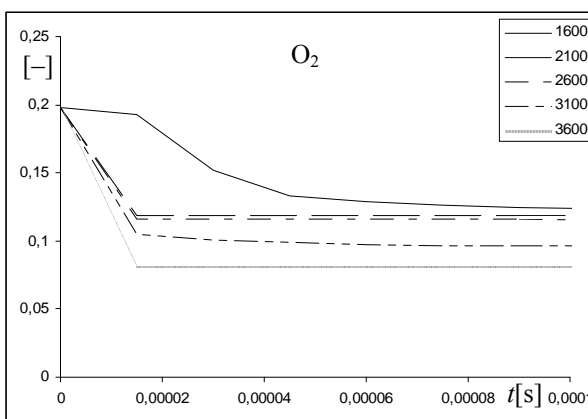


Fig. 2. Mole fractions of O_2 for $p=4MPa$, $X=10g_{H_2O}/kg$ of air, $\lambda=2,5$ and changed temperature

According to presented results fastest reactions, responsible for mole fractions of O_2 , H_2O and CH_4 for chosen thermodynamic parameters obtained after the 6ms. Further chemical reactions result only minor changes in the mole fractions. After about 17ms, the combustion process of CH_4 is complete. The relatively low temperature of the combustion process is not conducive to the formation of compounds from the group of nitric oxides, that is why the maximum mole fraction of NO_2 in the mixture is 2×10^{-11} and graph for this chemical species coincides with x-axis of the coordinate system.

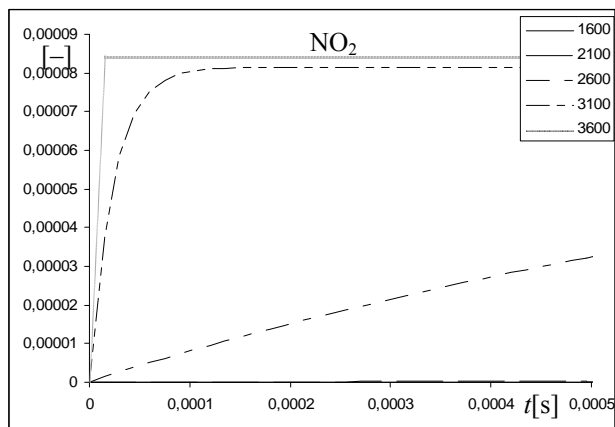


Fig. 3. Mole fractions of NO_2 for $p=4MPa$, $X=10g_{H_2O}/kg$ of air, $\lambda=2,5$ and changed temperature

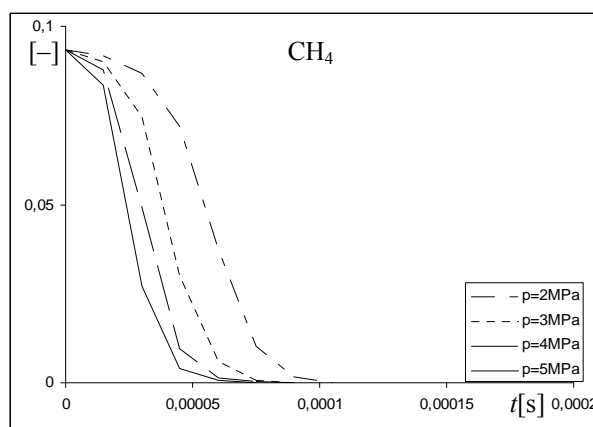


Fig. 4. Mole fractions of CH_4 for $T=1600K$, $\lambda=1,0$, $X=10g_{H_2O}/kg$ of air and changed pressure

Figure 2 shows the loss of O_2 from the initial mole fraction value. With the increase in temperature of the process followed to faster obtain the equilibrium fraction of O_2 . The relation between forward and reverse constant rate of reactions influence on the value of equilibrium fractions of chemical species, which in turn is influenced the prevailing temperature of the combustion process. According to Figure 3 increase in temperature of the combustion process favors the formation of compounds from the group of nitric oxides. Our results are qualitatively consistent with the data in available literature [5].

Figure 4 shows the effect of pressure on the combustion process on the example of the mole fractions of CH_4 . During the course of the combustion process the mole fraction of this species decrease. The mole fraction equal zero comes at a time that is shorter the higher is pressure of the combustion process. According to the results the speed of the CH_4 combustion is proportional to the prevailing pressure. Effect of pressure on the rate of chemical transformation is associated with the reactions that cause changes the quantity of substances (synthesis reactions and reactions of breaking chemical species) [10].

Figure 5 presents the effect of humidity of air on the water content in the combustion mixture. The figure shows that increase of humidity in air results the increase of water content in the mixture. It should be noted that, during the combustion process hydrogen-containing components of fuel combust, inter alia, to water form, thus the amount of water in the combustible mixture during the combustion process increases. The effect of humidity of air on water content in the combustion mixture is visible especially at high values of excess air-fuel ratio.

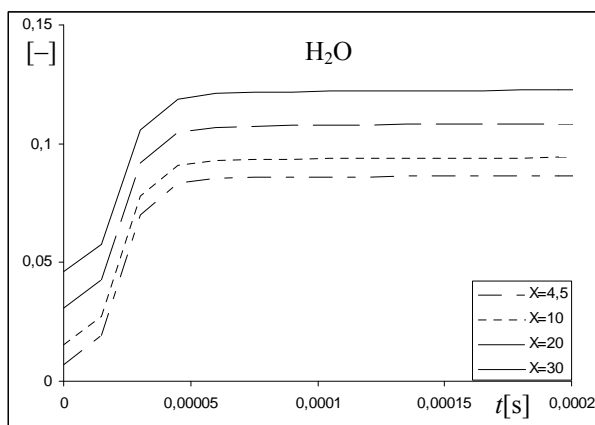


Fig. 5. Mole fractions of H_2O for $p=5MPa$, $T=1600K$, $\lambda=2,5$ and changed humidity of air

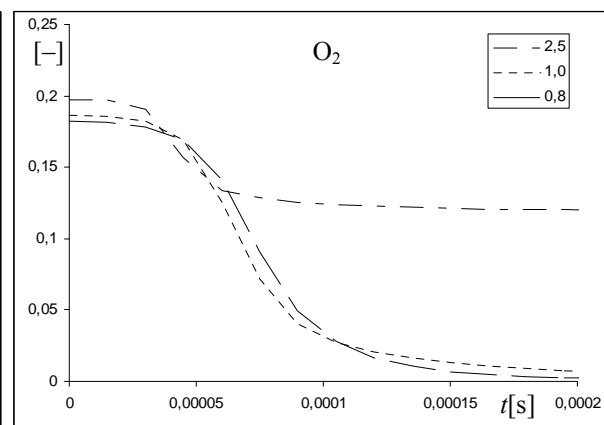


Fig. 6. Mole fractions of O_2 for $p=2MPa$, $T=1600K$, $X=10g_{H_2O}/kg$ of air and changed air-fuel excess

The content of the air in combustion mixture has a significant influence on the process of combustion. According to the data in figure 6 the combustion process is fastest in the case of a large excess of oxygen, while running slowest in the case of oxygen deficiency. It should also be noted that the value of air-fuel excess ratio is determined by the participation of oxygen mole fraction at the end of the combustion process.

Figure 7 shows examples results of the total heat release, derived from the CH_4 combustion. According to presented dependencies increasing pressure causes the acceleration of the combustion process and generates larger maximum heat release. The maximum heat release followed after 4ms from start of the combustion at 5MPa pressure and more than 11ms for the combustion at 2MPa pressure at the same temperature. Completion of the combustion process takes place after a 9ms and 20ms, respectively. A similar relationship was obtained in the case of temperature changes and constant other thermodynamic parameters.

Figure 8 shows the effect of water content in air at the speed of the combustion process. Due to imperceptible differences between individual results graph has been enlarged at the area of the maximum energy. The reference area is lowest graph from the Figure 7, which corresponds to the graph of the Figure 8 for relative humidity equal $10\text{g}_{\text{H}_2\text{O}}/\text{kg}$. According to results, increasing humidity of air decreases the maximum energy but accelerates the combustion process.

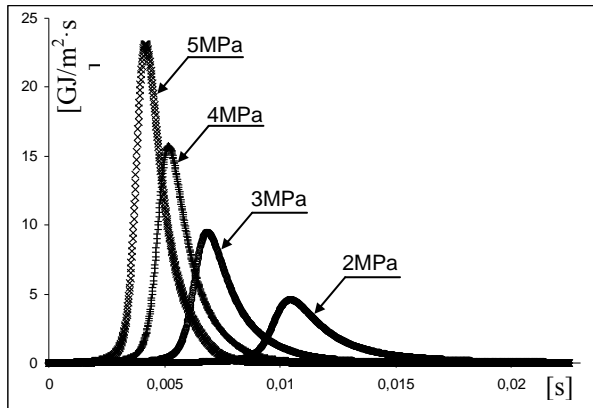


Fig. 7. The heat release from combustion process for $T=1100\text{K}$, $X=10\text{g}_{\text{H}_2\text{O}}/\text{kg}$ and $\lambda=0,8$ and changes pressure

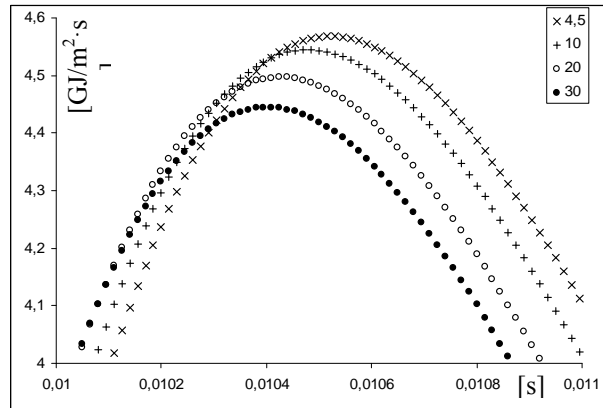


Fig. 8. The heat release from combustion process for $T=1100\text{K}$, $p=2\text{MPa}$ and $\lambda=0,8$ and changes humidity of air

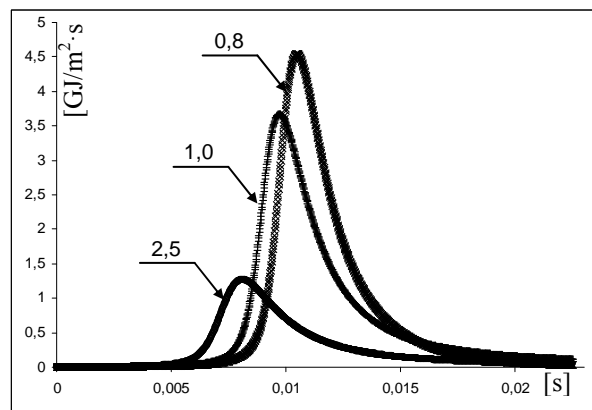


Fig. 9. The heat release from combustion process in $T=1100\text{K}$, $p=2\text{MPa}$, $X=10\text{g}_{\text{H}_2\text{O}}/\text{kg}$ and changes air-fuel excess ratio

Figure 9 shows the effect of the amount of air on the heat release. Increasing of air content in the mixture causes a significant drop of the maximum heat release but accelerates the combustion process.

4. Conclusions

As a result of calculations of methane combustion process it is possible to formulate the following conclusions:

- results of the kinetic calculation of mole fractions of chemical species considered in the GriMech 3 combustion process mechanism are qualitatively consistent with the data available in literature;
- increase in temperature of the combustion process favors the formation of compounds from the group of nitric oxides;
- the speed of the combustion is proportional to the prevailing pressure;

- increase of humidity of air results increase of water content in the mixture;
- increasing pressure and temperature of combustion process causes the acceleration of the combustion process and generates larger maximum heat release;
- increasing humidity of air and it's content in combustion mixture decrease the maximum heat release and accelerate the combustion process.

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