Features of methane-hydrogen mixtures combustion in oxy-fuel power cycle combustion chamber

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Abstract. The paper is focused on the study of features of methane-hydrogen mixtures combustion in an oxy-fuel power cycle combustion chamber. The goal of the study is to find optimal combinations of thermodynamic parameters, allowing to bring the fundamental combustion characteristics, such as the normal flame propagation rate, the adiabatic combustion temperature, and the ignition delay time, closer to the parameters that are characteristic of traditional gas turbine plants. The research method includes digital experiments in the Chemkin-Pro software package using detailed kinetic patterns. The key features of the fuel combustion process in oxy-fuel power cycle combustion chambers are changing the diluent medium from atmospheric nitrogen to carbon dioxide, which is the working medium in the cycle, and applying a supercritical pressure (about 300 atm). Both changes negatively affect the combustion process intensity. To achieve the normal flame propagation rate and the maximum adiabatic temperature that are acceptable for the possible flame stabilization in the combustion zone, to exclude uneven heat release and large values of chemical underburning, the amount of CO\textsubscript{2} diluent in the combustion zone shall be within the range of 10 to 20 % of the total amount of CO\textsubscript{2} supplied to the combustion chamber.

1. Introduction
According to the energy strategy of the Russian Federation, the list of activities to achieve the national goals and to address the strategic targets includes: "developing the hydrogen production and consumption; joining the ranks of the world leaders in its production and exports by the Russian Federation". Hydrogen energy technology should play there a special role. It is expected that hydrogen, that is used today mainly in the chemical and petrochemical industries, would be a new energy carrier replacing hydrocarbon energy carriers to create a "hydrogen-based economy".

However, one of the current trends in the development of modern large-scale energy technology is developing new energy cycles aimed at significantly reducing the harmful environmental effects of thermal power plants, with oxygen combustion using supercritical carbon dioxide (CO\textsubscript{2}) with an initial cycle temperature \( t_0 = 1 \text{ 100 to 1 400 °C, a pressure } p_0 = 25 \text{ to 35 MPa, an efficiency } \eta = 55 \text{ to 60 %, and "zero" emissions of harmful substances. CO}_2 \text{ is relatively inexpensive, available, non-toxic, less aggressive towards structural materials, and thermally stable within a wide temperature range (up to 2 000 °C). The transition to using CO}_2 \text{ as a working medium in the cycles of closed-type heat engines will allow to resolve the problems related to the specifics of using a water heat carrier, while obtaining an equal or even slightly higher efficiency within the same temperature range or significantly enhancing the efficiency by increasing the initial cycle temperature [1].} \)
To implement such cycles, we need to solve several scientific and engineering problems, including the development of theoretical foundations for creating power equipment operating on supercritical carbon dioxide, in particular, the design of a combustion chamber [2-3].

A change in the component composition and thermodynamic parameters of the working medium leads to a change in the type of combustion process. In an Allam cycle combustion chamber, combustion of natural gas with oxygen occurs in an environment of CO\textsubscript{2} diluent at a pressure of about 300 atm, which makes its working conditions very different from those in traditional gas turbine combustion chambers, where the pressure does not exceed 30 bar and the diluent is atmospheric nitrogen. In addition, it is necessary to evaluate the effect of adding hydrogen to the fuel because, despite the obvious environmental benefits, its use in the power engineering is currently at the stage of experimental research [4].

Four main parameters of a diluent determine its effect on the combustion process [5-9] and the presumable effect of changing the diluent from N\textsubscript{2} to CO\textsubscript{2}:

- Specific heat capacity. It determines the adiabatic flame temperature (in the active combustion zone, the temperature is close to adiabatic) which, in turn, largely determines the rate of reactions. All other parameters being equal, the flame temperature in a diluent medium with a higher heat capacity will always be lower. The specific heat capacity of CO\textsubscript{2} is higher than that of N\textsubscript{2} by 7 to 10%.

- Diffusion coefficient. It has a noticeable effect on the combustion process in case of a diffusion flame, when the rate of chemical reactions is largely determined by the diffusion of fresh fuel and oxidizer into the reaction zone. The diffusion coefficient of CO\textsubscript{2} is lower than that of N\textsubscript{2} by about 25%.

- Non-inert nature of CO\textsubscript{2} as compared to N\textsubscript{2}. Nitrogen is a low reactivity gas that does not participate in the chain of fuel oxidation reactions, except for the production of its oxides in small amounts. While CO\textsubscript{2} enhances the reactivity of the OH radical, there are reverse reactions CO+OH$\leftrightarrow$CO\textsubscript{2}+H and recombinations 2H+0.5O\textsubscript{2}$\leftrightarrow$H\textsubscript{2}O, which, in turn, entails a risk of high chemical underburning values.

- Radiating capacity. Carbon dioxide is a triatomic radiant gas; it can absorb heat and participate in radiation heat exchange, contributing to heating a fresh mixture of fuel with an oxidizer. This is the only parameter that contributes to the combustion process intensification.

It is clear that carbon dioxide is an inhibitor of chemical reactions. With volume content of diluent in oxidizer 79% the maximum drop of normal flame propagation rate is 4 times for methane and 3.8 times for hydrogen within the range of the oxidant consumption coefficients 0.7-1.4.

The curves in figures 2 and 3 show a characteristic difference between methane and hydrogen as fuels. $U_n$ of hydrogen is about 9 times higher, all other things being equal. This indicates a high reactivity of hydrogen as a fuel and is explained by a large number of active OH, H, and O combustion centers. In addition, you can see that methane is characterized by a maximum value of $U_n$ in the region of the oxidizer consumption coefficient equal to 1.05; whereas the same value of hydrogen increases over the entire range of values $\alpha$ under consideration. The maximum laminar flame propagation rate for hydrogen when burning with air is reached closer to 2.0 [10]. This difference is due to the fact that hydrogen has much larger ignition and combustion limit values, as well as different values of the Lewis number for the reaction mixture. The Lewis ($Le$) number determines the ratio between the thermal conductivity and the diffusion coefficient. The maximum combustion rate is achieved at $Le = 1$. Figure 3 shows a dependence graph of the normal flame propagation rate for fuel compositions with 10 to 90% hydrogen content.
There are 3 regions on the curves: the methane predominance region, the transition region, and the hydrogen predominance region. When moving towards higher hydrogen content, the curve slope gets steeper. The existence of three regions is due to the competition between the hydrogen production in the branched chain of methane oxidation and the hydrogen consumption in the chain of its oxidation as a primary fuel. In the methane predominance region, the hydrogen fraction increases in the course of combustion, and then, it is consumed, resulting in the limitation of hydrocarbon decomposition reactions and to some inhibition of hydrogen consumption reactions.

Having studied the graphs in figures 1-3, we can conclude that, CO\textsubscript{2} is an inhibitor of chemical reactions, which significantly reduces the flame propagation rate, whereas adding hydrogen to the mixture increases it. A supercritical pressure also has an inhibiting effect on the combustion intensity. A sharp decrease in the normal flame propagation rate is recorded in the pressure range of up to 10 atm for methane and up to 20 atm for hydrogen; then, the curve is virtually straight.

The above calculations show that the fundamental parameters of the combustion process are strongly dependent on a combination of various factors, which can be divided into:

- Factors dictated by the energy cycle for which the combustion chamber is designed (pressure, type of diluent, type of oxidizer, temperatures of the reacting components at the combustion chamber inlet).
- Factors varying during the design (distribution of diluent flows in the chamber volume; CH\textsubscript{4}/H\textsubscript{2} ratio in fuel).

Hence, the goals of our study are as follows:

- To determine the main parameters of chemical kinetics (the normal flame propagation rate, the ignition delay time, the adiabatic combustion temperature depending on the hydrogen fraction, the amount of diluent, and the fuel composition in the Allam cycle combustion chamber).
- To find optimal combinations of parameters; as an optimization criterion, we have selected achieving parameters close to the operating conditions of existing gas turbine combustion chambers, which will allow to rely on well-known design techniques when designing a combustion chamber.
2. Materials and methods

Figure 6 shows a schematic diagram of the Allam cycle combustion chamber. We will consider only the combustion zone marked by a red dotted line. The main goal is to determine the \( \text{CH}_4 / \text{H}_2 \) ratio in the fuel and the \( \text{CO}_2 \) diluent amount.

![Schematic diagram of the Allam cycle combustion chamber](image)

Figure 2. Drawing of the combustion chamber of the oxy-fuel combustion power cycle with distribution of \( \text{CO}_2 \) flows.

The initial data for determining the fuel and oxidizer flow rates that are required to heat the working medium to the initial cycle temperature are shown in table 1 [13].

| Component temperatures at the CC inlet, K | \( \text{CH}_4 \) | 645 | \( \text{CO}_2 \) flow rate at the CC inlet, kg/s | 543 |
|------------------------------------------|-----------------|------|--------------------------------------|------|
| \( \text{H}_2 \)                        | 848             |      | \( \text{Medium temperature at the CC outlet, K} \) | 1 373 |
| \( \text{O}_2 \)                        | 512             |      | \( \text{CH}_4 \) combustion heat, MJ/kg | 50.06 |
| \( \text{CO}_2 \)                       | 926             |      | \( \text{H}_2 \) combustion heat, MJ/kg | 120.08 |

The media heat capacity values at the given temperature and pressure values have been taken from the REFPROF database. The fuel consumption has been found using a simple heat balance Eq. (2):

\[
Q_{\text{phys CO}_2} + Q_{\text{phys O}_2} + Q_{\text{cal CH}_4} = Q_{\text{phys (CO}_2+\text{CP)}}
\]

(1)

Where \( Q_{\text{phys CO}_2} \) is physical heat of carbon dioxide at the combustion chamber inlet, kW; \( Q_{\text{phys O}_2} \) is the physical heat of oxygen, kW; \( Q_{\text{cal CH}_4} \) is the calorific value of methane, kW; \( Q_{\text{phys (CO}_2+\text{CP)}} \) is the physical heat of \( \text{CO}_2 \) and methane combustion products in oxygen.

The thermal power of the combustion chamber for heating \( \text{CO}_2 \) is 345 MW. The CC optimal maximum thermal power is considered to be 50 MW; therefore, we take the number of combustion chambers equal to 8, each with a thermal capacity of 43.125 MW.

The fuel and oxidizer consumptions are quite low (which is due to a significant contribution of the physical heat of the components to the incoming part of the heat equilibrium). A low consumption of the reaction components, as compared to the \( \text{CO}_2 \), leads to the fact that the \( \text{CO}_2 \) weight fraction in the combustion chamber varies within a range of 0.92 to 0.96, depending on the fuel composition. Therefore, for the study four values of \( \text{CO}_2 \) consumption in the active combustion zone were chosen: 10, 15, 20, 30 %.

To carry out the study, the reactor method for numerical simulation of combustion processes using the Chemkin-Pro software was used. With such an approach, the spatial inhomogeneity of the fields of concentrations, temperatures, and other quantities is either absent (ideal mixing reactors) or is solved in a one-dimensional formulation. This approach is used for a detailed study of chemical kinetics using combustion patterns with a large number of intermediates and reversible reactions which, in turn, allows to "capture" the changes in the combustion process due to the effect of external conditions. To determine the adiabatic combustion temperature the equilibrium reactor for calculating the chemical
and phase equilibrium was used. Closed homogeneous reactor was used for calculating ignition delay time and flame rate calculator was used for determining normal flame propagation rate.

According to the data presented in [12–14], the most adequate patterns for simulating the combustion under non-standard conditions are:

- **Mechanism No. 1 – GRI-Mech 3.0**, a mechanism designed to simulate the combustion of natural gas, including the calculation of a chemical underburning value. In its basic kinetics, this mechanism includes 53 intermediate reaction products and 325 reversible reactions of methane conversion into complete combustion products. According to [8], GRI-Mech mechanism shows a good convergence when simulating the combustion of methane and other hydrocarbon fuels. It was used in current study with a hydrogen content up to 40%.

- **Mechanism No. 2 – USC II** includes 325 components and 725 reversible reactions, as applicable to a wide range of combustion scenarios. The USC II model was developed based on the GRI-Mech 3.0 combustion mechanism, a hydrogen and carbon monoxide combustion model, and an integrated combustion model for ethylene and acetylene. The both models include the reaction rate data from recent topical studies.

### 3. Results and Discussion

For each fuel composition option, we determined the normal flame propagation rate \(U_n\) and the adiabatic combustion temperature \(T_{ad}\) at four flow rates of carbon dioxide supplied into the active combustion zone. The main results are shown in figures 3 and 4.

As expected, the normal flame propagation rate (figure 4) increases with an increase in the hydrogen fraction in the fuel. When the carbon dioxide content in the combustion zone is 30% of the total amount, the entire curve lies below the selected range. With a CO\(_2\) content of 20% and a hydrogen content of more than 82%, the value of \(U_n\) above 45 cm/s is reached. With a CO\(_2\) value of 10% and a hydrogen content of more than 35% the curve lies above the maximum value. Another important parameter is the adiabatic temperature of gases. The fact is that the temperature in the active combustion zone is close to the adiabatic one. To ensure the metal reliability according to the existing recommendations, it should not exceed 2 700 °C [15]. The upper limit of \(U_n\) – 90 cm/s – is relevant for full premix burner applications; the reaction mixture feed rate should be selected to prevent the flame flashback into the burner mixer.

The curve shapes in figure 4 are not obvious. With an increase in the hydrogen fraction, it was expected that \(T_{ad}\) will increase too. However, the family of curves reaches its minimum at the ratio of
\( \text{CH}_4/\text{H}_2 \) equal to 30/70. This is due to the fact that, at a given ratio in the fuel composition, the \( \text{CO}_2 \) weight fraction has a maximum value. According to the graph, only two points from the entire considered range are beyond the permissible adiabatic temperature value. The analysis of the graphs in the Figures shows that, for each fuel composition, we can select the amount of diluent that provides an acceptable flame propagation rate and adiabatic temperature in the combustion zone; whereas a shift in the fuel composition towards more hydrogen allows for the presence of a larger amount of diluent in the combustion zone.

To cover a wide range of hydrogen content in fuel for further research on the possibility of its use the points presented in table 2 were selected as operating ones. For the above points, we determined the ignition delay time in the Chemkin-Pro software; the results are shown in table 2. A decrease in the ignition delay time with an increase in the hydrogen fraction is due to an increase in the mixture reactivity, which also raises the question of creating a stable torch with no flashback [14].

| Calculation point | Fuel composition | Fuel flow rate, kg/s | \( \text{O}_2 \) flow rate, kg/s | \( \text{CO}_2 \) flow rate, kg/s | \( U_n \), cm/s | \( T_{ad} \), °C | \( T_{ig} \), sec |
|-------------------|------------------|----------------------|-----------------------|----------------------|----------------|----------------|----------------|
| 1                 | 0.9\( \text{CH}_4 \)+0.1\( \text{H}_2 \) | 0.88 | 3.55 | 8.83 | 54 | 2527 | 0.08 |
| 2                 | 0.5\( \text{CH}_4 \)+0.5\( \text{H}_2 \) | 0.54 | 2.39 | 10.19 | 52 | 2092 | 0.061 |
| 3                 | 0.1\( \text{CH}_4 \)+0.9\( \text{H}_2 \) | 0.41 | 2.54 | 13.58 | 54 | 1991 | 0.036 |

4. Conclusion

Our studies have shown that the range of the permissible amount of diluent in the active combustion zone is not high, amounting to 10-20\%. Its maximum amount is possible only with a hydrogen content in the fuel of at least 82\%, since, with a lower hydrogen fraction, the flame propagation rate is below the required minimum value. With a \( \text{CO}_2 \) content of 10\%, the extreme points – pure methane and pure hydrogen – have the maximum adiabatic temperature.

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