HEAT AND MASS TRANSFER
AND PHYSICAL GASDYNAMICS

Ignition of Multicomponent Hydrocarbon/Air Mixtures behind Shock Waves
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Abstract—Experimental and numerical investigations are performed of the temperature dependences of delays in the ignition, behind shock waves, of multicomponent mixtures simulating the products of steam conversion of methane. Experimental investigations are performed in the temperature range from 930 to 1880 K at pressures from 2.5 to 9 atm. It is demonstrated that ignition delays in mixtures of air with products of 50 and 100% steam conversion of methane may be described using the results of numerical calculations based on the known kinetic schemes of methane combustion. At the same time, a considerable (by a factor of two–three) reduction of delays in the ignition of methane/air mixtures during addition of steam is observed and discussed, which is not described by the known kinetic schemes. The obtained results may be used in developing hypersonic scramjet engines.

INTRODUCTION

The creation of a hypersonic aircraft (HA) is one of the promising trends in the development of aerospace technologies [1, 2]. A hypersonic scramjet engine (HSJE) with supersonic combustion, which utilizes atmospheric oxygen as an oxidizer, is considered for use as the HA propulsion unit. The problem of major importance in the HSJE development is the choice of fuel, with the determining factors being the cooling resource, the energy value, and the density of fuel in the tanks. From the theoretical standpoint, the optimal fuel is liquid hydrogen, which has the highest calorific value, an acceptable cooling resource, and minimal ignition delays; however, its practical application involves a number of serious disadvantages. First, its low density calls for a large tank volume, and this, in turn, brings about a considerable increase in the HA airframe resistance. Second, the need arises in a complex infrastructure for the production, storage, and transportation of liquid oxygen, and for fueling with liquid oxygen. In addition, this places higher requirements on the safety of HA operation.

Hydrocarbon fuels under conditions of high heat loads (flight Mach number of more than eight) are inefficient as cooling agents and inferior to liquid hydrogen as regards their energy value. However, of methane and other simple hydrocarbons of this series may be regarded as alternatives to hydrocarbon fuel because of their availability and of a relatively low cost both of fuels proper and of the entire infrastructure. The central problems include those of raising the cooling capacity and reducing the ignition delays of hydrocarbon fuels which may be used in HSJE. A possible way of overcoming these problems is using the process of steam conversion of methane (\( \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} – 226 \text{ kJ/mol} \)) on board an HA [3, 4]. The high endothermicity of the reaction and significant yield of hydrogen [5] lead one to expect an adequate cooling resource and calorific value of the fuel. In this case, a multicomponent gas mixture consisting of \( \text{H}_2, \text{CO, CO}_2, \text{CH}_4 \) and \( \text{H}_2\text{O} \) is delivered into the HSJE combustor; this mixture reacts with hot air that passed through a supersonic diffuser.

In treating the process of supersonic combustion in HSJE, some of the most important parameters include the initial temperature of the combustible mixture at the combustor inlet and the total time of combustion. The efficiency of a heat engine is known to be proportional to the temperature difference at the combustor inlet and outlet. Accordingly, when the initial temperature decreases (the final temperature for concrete fuel has a limiting value), the engine efficiency increases; this enables one to raise the thrust with the same flow rate of fuel, as well as to reduce the heat load in the inlet section. However, the decrease in the inlet temperature is accompanied by a considerable increase in the total combustion time, which defines the length of the combustor and, consequently, the weight of the propulsion unit and the loss of thrust due to wall friction.

The determination of the total combustion time at different temperatures and pressure for each concrete mixture calls for special study. The actual time of combustion is made up of two components, namely, the ignition delay and the fuel combustion time proper. While the fuel combustion time is mainly defined by the properties of fuel, the ignition delay depends largely on the temperature and pressure in the flow. These dependences are most pronounced in the vicinity of...
The processes of ignition and combustion of hydrocarbon fuels behind shock waves were studied by numerous researchers (many of those studies are referred to in the review by Zamanskii and Borisov [7]). However, no oriented studies supported by experimental data were performed heretofore on the kinetics of ignition and combustion of multicomponent mixtures, which are promising for use as fuel for HSJE, as well as of the effect on such mixtures from promoting additions and of energy stimulation leading to the reduction of ignition times.

In view of the foregoing, one can state that the investigation of the combustion of hydrocarbon-based multicomponent mixtures, the determination of the correlations between the ignition and combustion times, and the search for methods of controlling this process present an urgent problem involved in the development of HA.

This paper deals with the results of study of the mechanisms of ignition, behind shock waves, of the products of methane conversion in air in the low-temperature region.

**CHOICE OF KINETIC MECHANISM**

The initiation of ignition in supersonic flows presents one of the key problems of hypersonic internal aerodynamics. Of great importance in addition to purely hydrodynamic approaches (such as varying the flow geometry, improving the mixing of fuel with oxidizer, and so on) is the optimization of the reaction kinetics in the induction zone.

Note that the solution of such a multiparameter problem is possible only if the volume of experimental investigations is restricted to a reasonable extent, which is directly associated with a correct choice of a fairly simple kinetic mechanism used for numerical simulation. At present, detailed kinetic mechanisms of combustion have been developed for hydrogen, carbon monoxide, and the simplest hydrocarbons. The most complex of these mechanisms are used to describe the combustion of hydrocarbons; in the general case, these mechanisms must include both radical reactions and the combination of elementary stages of formation of both lighter and heavier hydrocarbons.

Dautov and Starik [8] presented the kinetic scheme of combustion of a methane/air mixture, which consists of 433 reversible reactions and includes the formation of different hydrocarbons from C₁ to C₂H₄ inclusive. This mechanism is characterized by good agreement with experiment as regards the characteristic times, temperature, and concentration of products, including nitrogen oxides and cyanides. However, this scheme is too complex for the purposes of our study; therefore, in analyzing the obtained experimental data, we used its reduced option containing 72 pairs of direct and reverse reactions recommended by Dautov and Starik [8] for the calculation of the ignition delay times. For better comparison of the possibilities offered by different schemes, we also used the GRI-Mech 3.0 scheme [9] describing the combustion of CH₄-C₂H₄ hydrocarbons. The calculations were performed using CHEMKIN II computer codes.

Figure 1 gives the predicted dependence of the total combustion time for some fuel/air mixtures on the initial temperature at the inlet to the combustor of an HSJE. The fuels are provided by methane, ethane, and a mixture formed at different degrees of steam conversion of methane, namely, Z = 20, 50, and 100%. By the degree of conversion Z is meant the percentage of the product yield of the CH₄ + H₂O → 3H₂ + CO reaction. The total combustion times for these fuels are related to the total combustion time of hydrogen as the shortest time. It follows from Fig. 1 that, as the temperature is reduced to values of 1000–1200 K acceptable for the HA structure, the time of combustion of hydrocarbon fuels increases considerably compared with that for hydrogen. These data lead one to conclude that efficient methods of reducing the total combustion time must be found if hydrocarbon fuels are to be used.

As was already indicated above, the total combustion time may be divided into the ignition time and the combustion time. The combustion time depends largely on the thermodynamic parameters and the type of fuel, while the ignition time amounting to the greater part of the total combustion time depends on the ratio between the rates of initiation and branching of chains, on the one hand, and of their break, on the other hand. This may be used to affect the ignition time by varying the reaction kinetics.

For example, the results of analysis of the ignition kinetics of an H₂ + O₂ mixture behind shock waves in the low-temperature region (see [10]) have demonstrated that the ignition delay is very sensitive to the concentration of oxygen atoms. So, an addition of 10¹³–10¹⁴ cm⁻³ of O atoms into a 10%H₂ + 5%O₂ + 85%Ar mixture at the initial moment of time at P ~ 1 atm and T ~ 800 K reduces the ignition delay by a factor of almost ten (see Fig. 2). One can mention several different methods for generation of active centers behind the