

# Investigation of macrokinetic parameters and flame propagation limits in a gas diesel

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**Abstract.** The work shows that the most important property of a flame is its ability to propagate in a combustible mixture in the form of a combustion wave. It has been proved that flame propagation is characterized by critical phenomena, when in certain cases minor changes in pressure, temperature or concentration can dramatically change the rate of the process. The concentration limits of flame propagation and the concentration limits of ignition are considered, depending on the presence of additives, the effect of which can be positive (promotion, expansion of limits) and negative (narrowing of limits, inhibition). The results of calculating the concentration limits of methane flame propagation in a stoichiometric fuel-air mixture and in a fuel-oxygen mixture are presented.

## 1 Introduction

It is well known that the most important property of a flame is its ability to spread in a combustible mixture in the form of a combustion wave. This fundamental property of combustion process is associated with extreme phenomena in gases burning in a gas diesel cylinder, as well as detonation or unsteady flame propagation [1-3].

The theory of flame front propagation should allow calculating the flame velocity, which is necessary for thermal engineering calculations. But a large number of theoretical approaches make it possible to solve the problem only for a flame in which the parameters of the chemical process of fuel transformation are quite simple. For a flame with more complex kinetics, it is practically very difficult to obtain a sufficiently accurate analytical solution. In this regard, the further development of combustion theory follows the path of numerical methods [4-6]. Currently, there is enough research in this direction. However, it should be noted that so far there is no exact satisfactory solution for the freely propagating wave of hydrocarbon combustion. In early studies, when the rate of the chemical process at the "cold" front boundary was assumed to be zero, it is difficult to imagine the effect of hydrodynamic processes on the chemical mechanism of combustion in a flame with a complex chain reaction [7-8].

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## 2 Methodology

The distribution of velocities in the gas flow of the diesel cylinder depends on the length of the torch, diameter, mass flow of gas, viscosity and thermophysical parameters of the combustion chamber. The jet of the gas mixture will have a parabolic velocity distribution.

The velocity value at a distance  $r$  from the center of the nozzle of the nozzle nozzle with radius  $R$  at a volumetric flow velocity  $V$  is equal to:

$$u = \frac{2V}{\pi R^2} \left(1 - \frac{r^2}{R^2}\right).$$

Assuming that the gas in the combustion chamber is close to a state of rest, then when sprayed through the nozzle of the nozzle, an almost uniform velocity distribution is obtained. But this is just an assumption, in reality, among the causes leading to the curvature of the front, or even the disintegration of the flame into parts, in addition to the effect of convective accelerations or thermal expansion of combustion products on the front, the effect of thermodiffusion stratification of the mixture occupies an important place. This effect consists in the fact that the reaction zone is depleted by light particles, which, due to thermal diffusion, flow into areas with a higher temperature [9-11].

It is more difficult to determine the normal combustion rate by the track method. The idea of the method is to photograph tracks of incandescent solid particles injected into the flame. The speed is determined by the exposure time and the length of the tracks obtained in the photo [12].

Combustion rate depends on the concentration of the oxidizer in the mixture, pressure and temperature, and the concentration of impurities. The nature of the fuel also has a noticeable effect on  $u_n$ , since low-atomic gases have maximum velocity values. The presence of multiple bonds in the fuel molecule also leads to large values  $u_n$ . The rate of combustion of hydrocarbon molecules with a branched structure is slightly lower than that of hydrocarbons of normal structure. The normal rate of methane combustion is higher than the rate of combustion of polyatomic hydrocarbons, which is probably due to the high value of the  $C-H$  bond energy [13-15]. Thus, the activation energy of the methane combustion process is of the greatest importance among hydrocarbons. Combustion dependence of the normal combustion rate on the composition of the mixture (under normal conditions) usually has a bell-shaped appearance. The exception is acetylene, the mechanism of transformation of which changes during the transition to rich mixtures [16-18].

Pressure, as well as temperature, have a complex effect on the combustion rate of mixtures of different compositions. For hydrocarbons, this is due to the transition to cold or blue flames when the pressure decreases, which are characterized by new macrokinetic parameters. Thus, with an increase in pressure from  $3.3 \cdot 10^{-3}$  to  $8-9.3 \cdot 10^{-2}$  MPa, the combustion rate of hydrocarbons, as well as CO and CS<sub>2</sub>, decreases by 15-30% [19].

Since these measurements were carried out in closed vessels, it is feared that the gas surrounding the flame diffuses into the reaction zone. Regarding the diffusion of air or even pure oxygen, Byrne [19] showed that it affects the value of  $u_n$ . The authors of the work [12] came to the same conclusion based on probe measurements of the outer cone of the propane flame in close proximity to its front. The weak effect of pressure on the combustion rate of carbon monoxide disappears completely in the range from 0.1 to 0.3 MPa when switching to its mixtures with oxygen.

The effect of temperature is more significant. Thus, for air mixtures of hydrogen and methane [16], the maximum  $u_n$  value for hydrogen changes 6.5 times with an increase in temperature by 410K, and for methane by 9.3 times with an increase in temperature by 660K. The phenomenological examination of the flame [12] established that the flame is the result of chemical and physical processes.

Therefore, the activation energy found by the temperature dependence  $u_n$  is a macrokinetic parameter of the front, and not the activation energy of only the chemical

process of fuel transformation in the reaction zone. Accordingly, it is impossible to determine the total reaction order from the dependence of  $u_n$  on concentration. All kinetic parameters set by  $u_n$  are only effective values. Based on the dependence  $u_n$  on pressure, the results of determining the effective order of the process  $1 < n < 2$  are known, and the propagation of the flame front of methane proceeds with the highest energy costs.

### 3 Results and discussion

Flame propagation is characterized by critical phenomena, when in certain cases minor changes in pressure, temperature or concentration can dramatically change the rate of the process. The values of the pressure concentration and temperature at which such a speed jump is possible are called critical, or limit values. For example, there are ignition limits and flame propagation limits, which mean that outside of certain intervals of change in the concentration of the combustible component (pressure) and temperature, ignition of the mixture is impossible, or the ignition that has arisen is not able to spread [20, 21].

The inability of combustible gases to ignite under certain boundary conditions does not mean, of course, that the reaction rate is zero. In fact, some stationary process is observed, during which the amount of heat released in the reaction turns out to be insufficient to balance the process of heat removal to the walls of the cylinder or towards the fresh mixture. As a result, the process slows down sharply at a short distance from the ignition site. The theoretical interpretation of the thermal theory of limit phenomena was proposed by Ya B Zeldovich [22]. He proposed a theory of flame propagation limits based on the dependence of the front temperature on its propagation velocity, taking into account heat losses and the Arrhenius dependence of the front propagation velocity on the combustion temperature. Combustion found that combustion temperature drop is  $RT_2/E$  at the limit, and the burning rate decreases by  $\sqrt{e}$  factor of one compared to its value in the absence of heat loss. If the flame spreads in the cylinder, then heat loss decreases with increasing diameter. Therefore, starting from a certain size of the cylinder, heat losses are determined only by radiation from the front. In this limiting case, Zeldovich obtained good convergence of the results of theory and experiment for the CO - air mixture. Heat loss was taken into account in the equations of conservation of mass and energy for A type  $A+B \rightarrow C$  reaction, along with Zeldovich, Spaulding and then Berlad, Yang, etc. They got similar results.

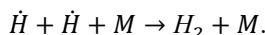
There are upper  $c_u$  and lower  $c_l$  concentration limits of flame propagation, at which the concentration of fuel in the mixture is minimal or maximum. Convective flows have a significant effect on the limits. It is known that when a flame spreads from bottom to top, the concentration range between the upper and lower concentration limits is wider than in the opposite direction of propagation.

Krivulin and other researchers [23] have shown that this area, when the flame spreads from top to bottom, narrows especially during overloads. It was found [24] that at a limiting pressure of 0.28MPa, a transition from convective quenching to stationary flame propagation occurs. When studying the mechanism of quenching by convective flow, the stretching of the front in the gas flow should be taken into account.

N.N. Semenov and his school discovered the phenomenon of chain ignition. If the chain reaction proceeds with branching, an increase in the rate of chemical transformation can occur even under conditions where the rate of heat release is less than the rate of heat transfer.

When the branched chain reaction reaches a certain critical speed, the thermal self-acceleration of the process begins, turning into an explosion. The method of generating active particles and the conditions of their existence are very important. When initiating a reaction, for example, with a heated wall, the induction time will be determined by the number of radicals generated as a result of initiation. The number of radicals is also determined by the volumetric and heterogeneous processes of death of these particles. At low pressures, when

the free path of the particles approaches the size of the combustion chamber, death on the walls prevails. With increasing pressure, a certain critical value of it occurs, followed by chain ignition (the first limit). With a further increase in pressure, the rate of recombination processes in the volume begins to increase. These processes are the result of triple collisions of radicals with stable molecules. The latter act as a thermal container, where the energy of two radicals or atoms is allocated:



Thus, at some pressure, a critical phenomenon occurs again (the second limit), beyond which there is no ignition. At pressures close to atmospheric, a third limit is found, which represents the beginning of the chain-thermal ignition region. In essence, this is a non-isothermal chain explosion. The active particles in this ignition region are radicals and atoms whose lifetime is shorter than the carrier particles of the chain at the first and second limits. The processes at the third limit proceed at significantly higher temperatures than at the first and second limits. It is clear that for us, considering the macrokinetic parameters and the limits of flame propagation in a gas-diesel cylinder, it is of course interesting to study the mechanism of processes starting from the third limit [25, 26].

Previously, the limits were found in a long pipe when the flame spread from top to bottom, vice versa and horizontally. These criteria have been adopted by scientists from the USA as a standard.

An empirical relationship is known between the concentration of fuel at the limits and the lowest molar heat capacity of the fuel  $Q_l$ :

$$c_l = \frac{2.2 \cdot 10^{15}}{Q_l}, \quad c_u = \frac{100}{(100 / c_l) - 1.42\alpha},$$

where  $\alpha$  – stoichiometric coefficient.

The lower concentration limits of flame propagation in complex combustible mixtures depend on the concentration of  $c_i$  components. They can be calculated according to the Le Chatelier rule:

$$c_l = \frac{100}{\sum_i (c / c_l)_i}.$$

Having carried out the calculation for methane used in gas diesel, the following results were obtained, presented in Tables 1 and 2.

**Table 1.** Concentration limits of methane flame propagation in a stoichiometric fuel-air mixture.

Fuel	$\alpha$	Temperature of combustion products	$c_l$ , %	$c_u$ , %
Methane	9.56	2320	5.0	15.0

**Table 2.** Concentration limits of methane flame propagation in a fuel-oxygen.

Fuel	$c_l$ , %	$c_u$ , %	$\frac{O_2}{O_2 + N_2}$ , %	$\frac{O_2}{O_2 + CO_2}$ , %
Methane	5.1	61	12.1	14.6

Concentration limits in mixtures are determined mainly by light fractions. An increase in pressure above atmospheric pressure significantly changes the concentration limits. Moreover, the effect of high pressure on the  $c_u$  of methane is special. With an increase in pressure to 40 MPa, the  $c_u$  increases from 15 to 46%. In general, the pressure contributes to the expansion of the ignition area by increasing the upper limit. This circumstance can be explained by the fact that with an increase in the fuel/oxidizer ratio at a constant temperature, it is possible that not hot, but low-thermal cold flames may occur, the area of existence of which is shifted towards high pressures. Thus, the  $c_l$  should decrease at elevated pressures.

The composition of the methane-air mixture at some limit value depends on the ratio of the diffusion coefficients of fuel  $D_F$  and oxygen  $D_{O_2}$ , characterizing the separation of the mixture and the formation of local areas in the vessel enriched with fuel or oxidizer. The mixture will be richer in stoichiometric at  $D_F < D_{O_2}$  and poorer at  $D_F > D_{O_2}$ .

The presence of multiple bonds in the fuel molecule significantly changes the course of the  $c_u$  dependence at a pressure of more than 0.1MPa, since the qualitative composition of the mixture changes. The temperature dependence of the limits is usually linear. An increase in temperature by 100 K lowers the lower limit of cm by 8-10%, and  $c_u$  increases by 12-16%.

The concentration limits of flame propagation, as well as the concentration limits of ignition, depend on the presence of additives, the effect of which can be positive (promotion, expansion of limits) and negative (narrowing of limits, inhibition). The positive effect exerted on  $c_u$  is usually associated with an increase in the calorific value of the mixture (additives: ethanol, propanol, etc.). Also, the ignition area can be expanded due to  $c_l$ . Such additives include chlorinated ethylene, fluoromethanes, etc.

The promotion and inhibition of the combustion process seem to have a common mechanism, since often an inhibitor at a certain critical concentration becomes a promoter. The use of inhibitors has been known for a long time. Of the early works on combustion inhibition, the review belongs to Bailey [27]. The work contains extensive material on the ignition of gases with additives of inhibitors. At that time, the search for anti-detonators to eliminate knocking in internal combustion engines was of interest. Further, interest in this phenomenon has grown significantly for the development of special means to ensure explosion and fire safety. Inhibitors have a certain selectivity of action on combustion process. For example, it has long been known that for the flame of CO, it is better to use chlorine gas or bromine as an inhibitor. For an oxygen - hydrogen and hydrogen - air mixture, hydrocarbons and halogenocarbons have maximum efficiency. The same inhibitors, for example, additives of methane or its halogen derivatives, do not suppress the combustion of diborane-oxygen mixtures. The ignition of a mixture of diethyl ether with oxygen is suppressed by primary and secondary alkylamines.

## 4 Conclusion

Combustion inhibition is caused not only by chemically active substances, but also by additives of inert diluents. However, in comparison with the number of chemically active inhibitors, the corresponding value of the inert impurity is 10-50 times greater. The role of inert impurities is reduced either to dilution of the mixture, or to increased heat removal from the reaction zone due to increased heat capacity and thermal conductivity of the medium.

Water vapor also has a certain effect on the ignition limits. For example, 29% of water vapor prevents the ignition of a methane-air mixture of any composition. This is more efficient than nitrogen or argon. But the most active additives for hydrocarbons are haloalkyls. Among them, the most common are chlorine, bromine and fluorine derivatives of methane or ethane, as well as some derivatives of bromine and iodine. The addition of CCl<sub>4</sub>, C<sub>2</sub>HCl<sub>5</sub>, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, C<sub>2</sub>HCl<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> to the methane-air mixture causes a decrease in the upper concentration limit, and the lower limit increases in the presence of these substances.

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