The formation of soot on the walls of the diesel combustion chamber and its effect on heat transfer in the cylinder

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Abstract. The presence of soot particles in the volume of the combustion chamber significantly increases the radiation of the flame and leads to an increase in local temperatures in the volume of the KS. Therefore, the presence of soot particles has a strong effect on the dynamics of heat generation in a diesel cylinder, especially at high load conditions. And an understanding of the mechanisms of its formation allows you to choose a way to reduce the soot content in the exhaust gas.

1. Introduction
One of the factors limiting the distribution of diesel engines in vehicles is the increased smoke content of their exhaust gases (EG). The smoke of the exhaust gas of diesel engines is directly determined by the content of soot particles in them. The presence of soot particles in the exhaust gas increases the toxicity of the exhaust gas as a whole, since carbon black has carcinogenic properties due to the adsorption of polycyclic aromatic hydrocarbons (PAH) on its surface. The mechanisms of their formation are still indisputable among specialists. The main interest for scientists is the initial stage of the formation of soot particles, associated with the formation of nuclei, from which soot particles are subsequently formed, and the associated phase transition from the gaseous state to the solid phase. In addition, the presence of soot particles in the volume of the combustion chamber (CC) significantly increases the radiation of the flame and leads to an increase in local temperatures in the volume of the CC. Therefore, the presence of soot particles has a strong effect on the dynamics of heat generation in a diesel cylinder, especially at high load conditions.

All the accumulated numerous experimental material on the influence of various factors on the dynamics of soot emission in diesel engines testifies to the close connection of the soot emission process with the indicators of the combustion process and, first of all, with the dynamics of heat release in the cycle. Comparing the change in the main indicators of the combustion process of various diesel engines with the change in the resulting soot emission, we can say that in all cases the concentration of soot particles in the cylinder reaches a maximum value almost simultaneously with the maximum heat release rate in the diffusion combustion section. The onset of carbon black always coincides with the onset of visible combustion and the onset of active heat. This means that soot in the diesel cylinder is formed immediately as soon as a stable flame front appears.

Internal mixture formation and pulsed diffusion combustion of a previously unmixed inhomogeneous fuel-air mixture in a diesel cylinder is always accompanied by the release of solid carbon in the form of soot particles, which determines the smoke of the diesel exhaust.
A significant decrease in exhaust smoke and soot concentration during the whole cycle is obtained with an increase in the amount of heat released during the homogeneous combustion of the air-fuel mixture prepared for the ELV and at the same time a decrease in the rate of heat release in the main phase of combustion, i.e. increasing the amount of fuel burning in the first phase of visible combustion, and reducing the amount of fuel burning in the diffusion phase. It should be remembered that these measures will increase the «rigidity» of the combustion process.

A significant amount of material has been accumulated in our country and abroad, which allows us to form certain views on the possible mechanisms of the formation of soot particles during the combustion of diesel fuel in the engine cylinder. There is no doubt that there is considerable heterogeneity in the torch volume both in the longitudinal and in the transverse direction, which makes it possible to identify a number of zones that differ in temperature and concentration of reacting substances. It has been established that the main reason for the intense soot emission during the diffusion combustion of a previously unmixed inhomogeneous mixture in the diesel cylinder is the existence of local zones with favorable conditions for pyrolysis reactions of fuel hydrocarbons. A necessary condition for the formation of soot is the presence of high-temperature and re-enriched zones in the CS, and their rapprochement and interaction, which also takes place in the diesel cylinder, is a sufficient condition [1].

2. Experimental part

In the process of turbulent diffusion combustion in a diesel cylinder, soot particles are partially formed and partially burned out by individual chemical-physical mechanisms. The concentration of soot in the engine cylinder at the time the exhaust valves are opened uniquely determines the exhaust smoke (assuming that soot does not burn out in the exhaust pipe) [2].

When fuel hydrocarbons enter the CC, they are decomposed with the formation of active radicals and acetylene when subjected to thermal action in the engine cylinder. Moreover, at temperatures below 1500 K, the formation of phenyl C₆H₅ and benzyl C₆H₃ radicals occurs through acetylene [3]. The resulting radicals interact with acetylene C₂H₂, C₂H radical and fuel hydrocarbons, which leads to an increase in the carbon fraction in the molecule, gradual dehydrogenation and the formation of a chemical nucleus of a carbon black particle.

According to the generally accepted and experimentally confirmed pattern of soot education, formulated and developed in the works of P. Tesner, at the first stage of the process as a result of volumetric homophase chemical reactions, a chemical nucleus of a carbon black particle is formed (C₂H, C₄H₂, C₆H₆). The physical nucleus of a soot particle is formed from it.

There is evidence that PAH are a precursor to the formation of soot particles in the diesel cylinder. In this case, the formation of PAH begins with the decomposition of the C₃H₄ radical or with the reaction of CH or CH₂ radicals with C₂H₂ acetylene molecules to form C₃H₃. They, in turn, can form the first aromatic ring (benzene molecule - C₆H₆).

Subsequent polycyclization of benzene formed according to this scheme is accompanied by the elimination of hydrogen and the association of phenyl radicals. It leads to the formation of polycyclic condensed hydrocarbons. The formation of plane condensed molecules from aromatic rings, apparently, is a chain radical process that proceeds through the intermediate formation of hydrocarbon radicals with a high degree of delocalization of the unpaired electron with their subsequent condensation:

![Figure 1](image-url)  
**Figure 1.** Intermediate formation of hydrocarbon radicals with a high degree of delocalization of an unpaired electron with their subsequent condensation.
Polycyclic hydrocarbons grow and move further to the periphery of the hydrogen present in them, the relative content of which is becoming smaller and smaller. Crystallites form, and the latter then combine into soot particles. When they collide, soot structures are formed [1].

The mechanism of elementary reactions of the growth of PAH from acetylene in surface growth reactions is also possible. The process begins with the addition of a C₂H₂ molecule to phenyl radicals to form a styryl radical. The addition of the second C₂H₂ molecule to the styryl radical leads to the closure of the aromatic ring and to the formation of a naphthalene molecule. Subsequent addition of C₂H₂ acetylene molecules to the aromatic ring leads to further growth of the molecule. Further growth of PAHs leads to the formation of soot particle nuclei.

The nucleation of soot particles is also possible through the formation of radicals as a result of the decay of diesel fuel molecules and their interaction. For instance:

$$2\text{CH}_4 \rightarrow 2\text{CH}_3 \rightarrow 2\text{C}_3\text{H}_8 \rightarrow 2\text{C}_3\text{H}_7 \rightarrow 2\text{C}_2\text{H}_4$$

$$\rightarrow 2\text{C}_6\text{H}_{14} \rightarrow 2\text{C}_6\text{H}_{12} \rightarrow 2\text{C}_6\text{H}_6 \rightarrow 2\text{C}_12\text{H}_{10} \rightarrow \text{C}_{42}\text{H}_{18} \quad \text{H T.D.}$$

Figure 2. The nucleation of soot particles through the formation of radicals as a result of the decay of fuel molecules and their interaction.

The formation of soot particles occurs in the combustion zone, where in a small volume they have a high concentration. Turbulent motion covers the entire volume of the cylinder, including the boundary layers and, naturally, turbulent diffusion is the main mechanism for the transfer of soot particles, i.e. particles are transferred from the volume of the formation focus to the surrounding area (i.e., into the volume of the cylinder), where the concentration of particles is much lower. As a result, their concentration in the cylinder is leveled. In addition to the transport velocity, the particles have a density different from the density of the gases in the cylinder, and due to inertial forces they move relative to the surrounding and carrying gas volumes. Since the particle sizes are significantly larger than the sizes of gas molecules, it is obvious that the thermal motion of gas molecules, causing molecular diffusion, does not affect their motion in a turbulent flow. Entering zones with an excess of oxidizing agent, soot particles begin to burn out and their concentration decreases.

Obviously, the quality of the distribution of the fuel and its chemical composition affects the rate of formation of primary soot particles, which is confirmed by many studies.

According to [4], intense soot formation is observed during the early phases of combustion, but already after the kinetic phase. The delay time between the initial heat release (which occurs in the kinetic phase) and the maximum heat radiation is the main period of the formation of high-temperature solid soot microparticles emitting thermal energy. The later diffusion phase of combustion is characterized by the oxidation of accumulated soot. The maximum value of the soot concentration is observed after a period of time equal to 15...20% of the total duration of the fuel combustion process.

When burning 1 kg of diesel fuel, an average of 3...5 g of soot is obtained. The sizes of soot particles are 0,01...1,0 nm. Visual observations using an electron microscope showed that the shape of the soot particles is close to spherical. Often they are grouped in an ensemble of several spherical particles resembling in appearance a cluster or a loose lump [5].

With a decrease in the injection advance angle, the concentration of soot can sharply increase, since this reduces its burnout time. In thermally insulated ICE, an increase in the temperature of the working fluid can lead to an intensification of the processes of formation and burning of soot. In this case, the maximum concentration of soot is significantly reduced at the end of the combustion process.

In fact, there is turbulent movement of the working fluid in the cylinder, which is a dispersed medium (gas, solid microparticles of soot, and also droplets of liquid fuel that have not yet had time to evaporate). Turbulent motion covers the entire volume of the cylinder, including the boundary layers.
and, naturally, turbulent diffusion is the main mechanism for the transfer of soot particles. The extension of the molecular diffusion mechanism that occurs in the laminar layers to soot microparticles is possible only if they obey the laws of Brownian motion. However, their motion is characterized by a relaxation of speed, and the laws of Brownian motion do not apply to them. It also means that if the boundary layer in the CC were laminar, then particles could penetrate through it and settle on the surface of the CC only if they obey the laws of Brownian motion.

Particle transport in a turbulent gas flow is accompanied by the formation of soot particles in the combustion zone, where they have a high concentration in a small volume.

Taking into account generally accepted concepts with a certain degree of certainty, it can be accepted that the interaction of carbon with gases is determined by the diffusion of the gaseous reagent to the surface of the soot particle, and the reaction itself proceeds on the external geometric surface of the sample; the reaction rate was assumed to be infinitely large. It can also be assumed that the reaction rate is finite and proportional to the concentration of the gas reagent. In addition, one can take into account the supply of matter to the particle surface due to diffusion. It can also be assumed that the interaction of carbon with oxygen occurs not only on the outer surface of the particle, but also in volume, that is, it is necessary to take into account the supply of matter to the inner surface of the particle.

There is evidence that the main factors affecting the oxidation of soot particles are time, temperature, and turbulence.

The reactivity of a mixture of fuel with oxygen at various temperatures, associated with the chemical kinetics of combustion. Since a decrease in temperature can reduce the rate of the oxidation reaction, and by the time the exhaust valve opens, soot particles may not have time to completely burn out even if there is enough oxygen for oxidation.

The rate of oxygen to reacting particles. And since there is turbulent movement of the working fluid in the diesel cylinder, the rate of oxidation of soot particles will depend on the actual rate of oxygen to the surface of the reacting particle, which is determined by the coefficient of turbulent diffusion.

A significant factor also affecting the intensity of oxidative processes is the value of the relative surface of soot particles. As a particle burns out, the value of its specific surface decreases; therefore, its oxidation rate also decreases [5].

It should also be taken into account that particles located near (at a distance of up to 2...3 mm) of the cylinder walls, the head of the block and piston have a much lower temperature and, accordingly, the oxidation rate. And, given that near the walls there is also a deceleration of turbulent pulsations, i.e. oxygen supply rate, such particles, as a rule, do not have time to burn out and fall into the exhaust gas.

The carbon formed in the flame may be gaseous, liquid or solid. As a result of this, the carbon oxidation process, in our opinion, can be homogeneous (at the molecular level in the gas phase), semi-heterogeneous (oxidation of the nuclei of condensed particles comparable with large molecules), and heterogeneous (oxidation of liquid and solid particles). In a general form, carbon oxidation occurs due to three total processes [1]:

- reactions of carbon with oxygen:
  \[ C + O_2 = CO_2 \]
  \[ 2C + O_2 = 2CO \]

- interactions with water vapor:
  \[ C + 2H_2O = CO_2 + 2H_2 \]
  \[ C + H_2O = CO + H_2 \]

- and interactions with carbon dioxide:
  \[ C + CO_2 = 2CO \]
Carbon deposition on the surfaces of CC, resulting from the incomplete combustion of fuel and oil film in oxygen-depleted zones, has a significant impact on the flow of the working process. In particular, it is known that in ICE with spark ignition the presence of soot can lead to premature ignition of the working mixture [9], and in diesels, to disrupt the process of mixture formation due to coking of the nozzle openings of the atomizer. As for studies of the blocking effect of soot on unsteady heat transfer between the working fluid and the surface of the internal combustion engine, there have been practically no such works until recently. In the 90s, research was conducted at the MSTU. N. Bauman, as well as at the Munich Technical University, as a result of which quantitative data were first obtained. In earlier publications [10-15], devoted to the study of the thermophysical properties of carbon deposits, mainly information on the heat-insulating effect of carbon deposits, which is not confirmed by experimental results, is provided.

It can be assumed that from the region of turbulent diffusion, which is a collection of vortices covering the particles of gas and soot, a soot particle with the highest energy breaks out. Leaving the vortex surrounding it, it moves until it hits the surface of the wall. Particles on the wall surface (i.e., the formation of carbon deposits) are most strongly retained in those areas where thin resinous-lacquer films are formed as a result of oxidation of fuel and oil. The roughness of the surfaces and the resinous-varnish film formed on them are the reasons for the adhesion of the first soot particles and the formation of an initial carbon layer, on which the next layer is applied in the same way, etc. The presence of soot particles in the boundary layer can affect the temperature profile and, consequently, the heat transfer from the working fluid to the wall. In addition, the particles directly transfer heat when moving in the transverse direction of the boundary layer.

The intensification of heat transfer in the presence of particles is determined mainly by three factors: a decrease in the thickness of the boundary layer; heat transfer in the collision of particles with the walls; a decrease in turbulent viscosity in the wall region.

A decrease in the thickness of the boundary layer is physically associated with some abrasive effect of particles on it [16-21]. This leads to an increase in the temperature gradient and intensification of heat transfer in the boundary layer, which is carried out mainly by thermal conductivity.

When soot particles collide with the walls, the heat transfer intensity depends on the nature of the contact of the particles with the surface. If a soot particle collides with the surface and immediately bounces, then the heat transfer is negligible. This is mainly how large particles behave [21-25]. Smaller soot particles, colliding with the surface, do not bounce off, but slip, while remaining in contact with the surface for a certain period of time. As a result of heat transfer, its temperature approaches the surface temperature. In this case, the residence time of the particle on the surface is important, however, it is obvious that the collision frequency will also significantly affect the heat transfer rate. The most favorable condition for heat transfer is created when a particle settles on the surface. Moreover, this behavior is more characteristic not for single particles, but for a group of particles concentrated in the form of separate clouds that settle on the surface for a long time.

A high concentration of soot particles, accompanied by coagulation, as a rule, suppresses turbulence. In this case, the turbulent viscosity increases due to the presence of particles and the heat transfer rate decreases. It is known that in the case of an extremely high concentration close to the maximum, the turbulence «freezes» [26-30]. It is obvious that, with a decrease in turbulent viscosity, heat transfer intensifies.

We emphasize that in all three cases we are talking about the influence of particles on convective heat transfer, in this case contact heat transfer with the wall and the thickness of the boundary layer play an important role. Any of these three cases can prevail at a certain point in time [31-33], since the particle flux is inherently unsteady (much more unsteady than a single-phase flow).

3. Conclusion

Thus, the presence of soot particles in the ICE working fluid, on the one hand, intensifies heat transfer in the boundary layers of the CS, and on the other hand, blocks heat transfer from the working fluid to its walls, forming a soot layer with a low heat penetration coefficient on the surface of the latter.
The extremely small thickness and fine structure of carbon deposits significantly complicate the application of methods for directly measuring the temperature on the surface of the layer itself, therefore, use non-contact (optical) methods. According to the results of studies, the maximum surface temperature of the carbon layer reaches 700 K and higher, which significantly exceeds the maximum temperature of the metal surface. In addition, in ICE with spark ignition, the amplitude of temperature fluctuations of the surface of the deposition layer substantially depends on the type of fuel, in particular, on the type of antiknock additives [31-33].

It is known from operating practice that the thickness of a layer of engine deposits cannot grow indefinitely; after a certain time of operation, the layer build-up stops and its thickness stabilizes. In accordance with the model described in [7], stabilization of the layer thickness ceases with the onset of the phase of the equilibrium state of soot, at which a dynamic equilibrium is established between the amount of substance passing into soot and burnout of the soot. As a result of increasing the thickness of the soot layer, the temperature on its surface rises and, at certain values of this temperature, new soot particles that get to the surface burn out to a greater extent. Only an insignificant part of them is deposited on the surface of the layer, the thickness of which stabilizes as a result. This assumption is also confirmed by the fact that in ICE with a high-temperature metal surface of a CC (with a temperature of more than 600 K), deposition is practically not observed.

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