Results of calculations of soot formation in a tractor diesel engine running on biofuel

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Abstract. When burning fuel in a diesel internal combustion engine, soot is an undesirable product. To reduce the soot content in the exhaust gases, it is necessary to know the physical and chemical bases of the process of soot formation and soot burnout. Due to the determining role of acetylene in the formation of polycyclic aromatic hydrocarbons in rich mixtures in the low-temperature zone and the key role of acetylene in the surface growth of a particle in the high-temperature zone, it is concluded that the rate of surface growth of a particle is proportional to the concentration of acetylene in the reaction zone, which can be determined by the gas-kinetic method, numerically solving a system of differential equations for the components of the gas mixture under consideration.

1. Introduction
In various fields of science, a lot of experience has been accumulated in studying the process of soot formation, although in some processes soot is the final target product of combustion. Despite this, the physical and chemical foundations of the process are largely similar and can be combined into a single theory for considering this complex multi-stage process.

The industrial soot obtained by the furnace method in reactors as a result of incomplete combustion of the hydrocarbon fuel sprayed by the nozzle with a turbulent air flow is the closest in terms of the formation conditions and the product burned to diesel soot. The analysis of the physical properties, composition and structure of soot particles, as well as the accumulated significant experimental and theoretical material of soot formation processes will allow us to look with confidence at the issues of reducing the soot content in the exhaust gases (EG) of diesel internal combustion engine (DICE) [1].

In the process of preliminary fuel reformation, soot particles of various sizes are formed in the DICE. The difference in size is explained by the heterogeneity of the conditions under which a particular local volume of gas decomposes. A significant dependence of the radiation of soot particles on their size determines the influence of the nature of the polydispersity of soot on the emissivity of the flame.
During the decomposition of hydrocarbons, a secondary soot structure may occur, which can be destroyed in a flame. Along with this, it is possible to crush individual particles that represent the primary soot structure. Therefore, there is reason to believe that the cause of increased flame radiation in the presence of intermediate fuel decomposition products containing hydrogen in the soot is a sharp increase in the total surface of the particles that occurs when both the secondary and primary soot structures are destroyed in the flame\cite{2}.

It almost never happens that there is completely no $CO_2$ and $H_2O$ in the flame and only oxygen is present. The structure of the reacting flows is very complex, since it is determined by the distribution functions of component concentrations, temperature, density and velocity. If the reacting flow is also turbulent, then all these values change not only in space, but also in time, which significantly complicates the determination of the interaction of fields of different quantities. The situation is particularly difficult in reacting turbulent flows, in which the rates of chemical reactions (and, accordingly, heat release) depend non-linearly on temperature.

The radiation properties of the flame depend on the size and unit concentration of soot particles suspended in the gas phase, and the combustible mixture cannot simultaneously reach a particular area and its individual micro-volumes can be heated in different ways. Therefore, carbon black is also present in the decomposition products along with intermediate products. Carbon black usually contains almost no gases in its composition (in some cases, only 2-3% of hydrogen is contained in soot), it burns without the release of volatiles. It was established that a significant grinding of soot in the process of its oxidation, in principle, occurs both as a result of intensive burning of all particles, and as a result of their crushing. Combustion soot particles takes place strictly in the kinetic mode, and for very small particles, the boundary layer near their surface is so insignificant that it will not have any practically diffusive braking during the oxidation process. Acetylene is actively involved in the formation of aromatic polycyclic aromatic hydrocarbons (PAH) rings, although the full kinetic model of PAH formation is still not precisely defined. The formation of PAH can begin with the decay of $C_3H_4$ or with the reaction of $CH$ radicals, or $CH_2$ with acetylene molecules to form $C_3H_3$ radicals, which are able to form the first aromatic ring (a benzene molecule $– C_6H_6$)\cite{3}.

### 2. Methods and Materials

It is proved that the presence of aromatic compounds can have a significant share, and the mechanism of formation of subsequent aromatic rings can take place with the participation of acetylene (figure 1).

Aromatic compounds can condense independently, forming high-molecular compounds. When the temperature exceeds 1000K, the aromatic ring is prone to destruction with the formation of more stable particles and radicals, including acetylene. At values below 1000K, according to the low-temperature mechanism, phenyl can act as a germ particle, in the formation of which acetylene is also involved:

\[
2 C_2H_2 \rightarrow C_4H_3 + H, \quad C_2H_2 + H \rightarrow C_2H + H_2, \quad C_2H_2 + C_2H \rightarrow C_4H_2, \quad C_2H_2 + C_4H_3 \rightarrow C_6H_5.
\]

Particle surface growth rate:

\[
C_{soot} + C_2H_2 \xrightarrow{k_h} C_{soot+2} + H_2,
\]

where $k_h$ - is the rate of the particle growth reaction.

The particle growth rate depends on the total surface area of the particles:

\[
k_h = 1.05 \cdot 10^4 \exp \left( \frac{-3.1 \cdot 10^3}{T_f} \right) \frac{1}{A} \left[ C_2H_2 \right].
\]

where $A$ - is the surface area of soot particles.
The dependence of the growth of the diameter of the soot particle on the increase in its mass:

\[
\frac{dD_p}{d\varphi} = \frac{1}{3} \left( \frac{6}{\rho \pi} \right)^{\frac{1}{3}} m_p^{\frac{2}{3}} \frac{dm_p}{d\varphi} .
\]  
(3)

We can assume that the soot particle consists only of interconnected carbon atoms and has a density of 1.9 g/cm³. At the same time, we assume that the density of the particle is distributed evenly over its volume [4]. Then the particle growth rate can be represented as:

\[
\frac{dD_p}{d\varphi} = 0.33m_p^{\frac{2}{3}} \frac{dm_p}{d\varphi} .
\]  
(4)

we will get:

\[ A = 3.15 \frac{m_p}{D_p} . \]  
(5)

The number of soot particles in the reaction zone may decrease as a result of coagulation and the transition of particles to the burnout zone. The rate of removal of particles from the formation zone is assumed to be proportional to the rate of heat release. The average diameter of the particles in the burnout zone:

\[
\frac{dD_p}{d\varphi} = \frac{dD}{d\varphi} + \frac{dD_{av}}{d\varphi} + \frac{dD_{c}}{d\varphi} .
\]  
(6)

In the process of coagulation, the mass content of soot remains constant. Soot agglomerates in the exhaust system of a DICE have a chain structure consisting of many spherical particles formed in the pre-flame zone. Although diesel soot is generally electrically neutral, it contains a relatively large proportion of the charged particles found in the flame. The distributed electric charge contributes to an increase in the coagulation rate in the oxidation zone. It is established that the process continues in the exhaust system. The speed of the process under consideration depends on the particle concentration, pressure and temperature conditions [5]. The speed of the Brownian coagulation process is determined by the expression:

\[
\frac{dN_p}{dt} = -k_k N_p^2 ,
\]  
(7)

where \(k_k\) - is the coagulation constant, \(N_p\) - is the unit concentration of soot particles.
Then the current amount of soot particles in a DICE can be determined from the equation

\[
\frac{dN_p}{d\varphi} = \frac{dN_f}{d\varphi} - \frac{1}{6n} k_k N_p^2,
\]

(8)

where \( n \) - is the speed of rotation of the diesel crankshaft.

Since, under conditions of high gas pressure in the cylinder of a DICE, the free path of the particles is comparable to the size of the particles themselves, the coagulation constant, taking into account the steric factor, can be determined by the expression:

\[ k_k = P_0 C_k \sqrt{T D} . \]

Then equation (8) can be written as:

\[
\frac{dN_p}{d\varphi} = \frac{dN_f}{d\varphi} - P_0 C_k \sqrt{T D} N_p^2 ,
\]

(9)

where \( P_0 \) - is the steric factor; \( C_k \) - is the constant coefficient of the coagulation rate.

Let's denote \( G \) - the mass of soot in the zone. The ratio of the mass content in the zone to the number of particles can be determined by the mass of the particle:

\[ m_p = \frac{G}{N_p} . \]

By logarithming and finding the derivatives of this expression, we get:

\[
\frac{d m_p}{m_p} = \frac{d G}{G} - \frac{d N_p}{N_p} .
\]

(11)

The expression (11) can be written:

\[
\frac{d m_p}{d\varphi m_p} = \frac{dN_p}{d\varphi N_p} .
\]

(12)

The value of \( \frac{d D_k}{d\varphi} \) during coagulation:

\[
\frac{d D_k}{d\varphi} = -\frac{1}{3} m_p^\frac{1}{3} \frac{dN_p}{d\varphi N_p} .
\]

(13)

Convert:

\[
\frac{d D_k}{d\varphi} = -\frac{1}{3} m_p^\frac{1}{3} P_0 C_k \sqrt{T D N_p} .
\]

(14)

Taking into account the assumptions about the constant density of the particle and the spherical shape of the particle, it is possible to strictly relate the mass and diameter of the particle, then the expression (14) can be written:
The results of numerical simulation of soot emission in the DICE running on methanol and methyl ether of rapeseed oil (MROME) are presented in figures 2-4.

3. Results and Discussion
In figure 2, a sharp drop in the average mass diameter of the particles is caused by an exponential increase in the number of particles formed in the pre-flame zone.

\[
\frac{dD_k}{d\varphi} = P_0 C_k D^{1.5} T^{0.5} N_p. \tag{15}
\]

The further growth of particles is the result of two opposite processes – gasification and carbon condensation. At the early stages of the particle evolution, the condensation rate significantly exceeds the gasification rate and the particle diameter increases very quickly. The graph reflects not only the process of surface growth and coagulation, but also the simultaneous appearance of new nuclei as fuel hydrocarbons enter the reaction zone.

4. Conclusion
The displacement of the combustion process of the MROME to the late angles of rotation of the crankshaft (r.c.s.) is also reflected in the rate of particle nucleation. It should be noted that the use of
MROME in a DICE reduces the number of particles in the cylinder by almost two orders of magnitude. The reaction zone is saturated with gases coming from the decomposition of methanol, which reduces the concentration of hydrocarbon raw materials for the formation of chemical precursors of soot - acetylene, propylene, etc.

![Figure 4. The concentration of soot in a DICE.](image)

As a result of the expansion of the reaction zone, the particle growth rate also decreases. Verification of the calculations made was carried out on the basis of experimental measurements of the smoke content of the exhaust gases of a DICE during experimental studies in various operating modes.

References

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