Formation and burning of soot particles in a diesel cylinder when working on ethanol-fuel emulsion

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Abstract. The chemistry of the processes of formation and burning of soot particles in a diesel cylinder is associated with a large number of chemical reactions and is very complicated. During combustion, the fuel supplied to the engine cylinder does not completely burn out. Complete combustion is hindered by a number of factors: the limited mixture formation and combustion processes in time, the imperfection of the fuel supply and atomization processes, and the uneven concentration of oxygen and fuel. So, with a lack of air and a high temperature of the air charge in the engine cylinder, the supplied fuel undergoes pyrolysis with the formation of products of incomplete oxidation: carbon monoxide, aldehydes, carboxylic acids, soot, and various heavy hydrocarbons. Soot has a large specific surface area, up to 75-80 m²/g, which leads to its high absorbent capacity. Therefore, when it settles in the engine’s exhaust system, soot absorbs unburned hydrocarbons like a sponge, forming black, ointment-like deposits. With increasing temperature of the exhaust gases, for example, with an increase in engine load, these deposits are prone to ignition.

The mechanism of soot formation is associated with a large number of chemical reactions and is very complex. In the general case, it is a sequence of processes of decomposition of hydrocarbon fuels, the formation of active carbon particles in a flame, the growth of soot nuclei, particle agglomeration and soot oxidation. The soot content in the exhaust gas (DG) of a diesel engine depends on all of the above processes, of which only the last has been most studied. Studies have shown that carbon particles form in the central zone of the fuel stream, where the oxygen content is insufficient.

The soot content in the exhaust gas depends on the properties of the fuel, the structure of the fuel flame, the shape of the combustion chamber, and flame temperature and is the result of two determining processes — formation and oxidation. These processes, in turn, depend on the design features of the engine and its operating modes [1-4].

In the research process, an ethanol-fuel emulsion (EFE) of the following composition was used:

- diesel fuel (DF) - 67.5%,
- ethyl alcohol - 25%,
- water - 7%,
- additive - 0.5%.

Figure 1 shows the possible chemistry of the process of soot formation in the cylinder of a 4F 11.0 / 12.5 diesel engine when operating on an EFE.

Ignition of fuel from compression in a diesel cylinder is complex and multi-stage. It is generally accepted that ignition of hydrocarbons mixed with air is of a chain-thermal nature. The speed of the preparatory processes depends on the propensity of the fuel to form active particles. When a diesel engine is operating on an EFE, alcohol and diesel fuel are injected into the cylinder simultaneously.
Vapors of alcohol are ignited by the flame of diesel fuel, the ignition of which occurs according to the traditional scheme [5-10].

Since carbon black is a metastable product of the combustion process, it is impossible to exclude the possibility of the existence of several transition paths (mechanisms) to this state, depending on the conditions of the combustion process. When a diesel engine is operating on an EFE, the majority of soot in the exhaust gas is formed during the combustion of diesel fuel. The features of soot formation during the combustion of diesel fuel in a cylinder are considered in detail in the works of many Russian and foreign scientists. We believe that the main mechanisms that make the most significant contribution to the formation of soot particles in the diesel cylinder are the low-temperature phenyl mechanism (NTFM), which prevails at temperatures below 1500 K, and the high-temperature acetylene mechanism (VTAM), which prevails at temperatures above 1500 K.

Ethanol has a significant impact on the processes of combustion, formation and oxidation of harmful substances in the cylinder. A significant role is played by the combustion characteristics of emulsified fuels and the thermal decomposition of ethanol with the formation of a significant amount of C2H5 and OH active radicals, which contribute to the intensification of combustion processes.

Consider a possible mechanism for the formation of soot from ethanol [11-13].

Ethanol is a representative of the homologous series of monohydric alcohols. When ethanol is burned, carbon dioxide and water are formed:

\[ C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad (1) \]

Significant charge heterogeneity is observed in the diesel cylinder throughout the process of fuel injection, combustion and expansion. The emission of solid carbon in the form of fine soot particles
during combustion can occur as a result of pyrolysis, as well as oxidative cracking of fuel molecules in zones of a highly over-enriched mixture, provided that the temperatures in these zones are quite high. It is these conditions that are created in diesels during the combustion of droplets of liquid fuel, when in some zones of the spray jet the local values of the mixture are close to stoichiometric and, accordingly, the flame temperatures are maximum, while in adjacent zones there is a significant lack of oxygen. Under such conditions, carbon can be released during the decomposition of an ethanol molecule [14-18].

Alcohols are characterized by higher burning activity compared to hydrocarbons. Due to this, combustion is more stable, and the ignition limit of the mixture is shifted to a poorer area. The main reason for this is the dissociation of ethanol at high temperatures. This leads to the formation of active radicals that facilitate the onset of a chain reaction and accelerate the process of fuel oxidation. In the temperature range 1000 ... 2600 K, the ethanol molecule undergoes thermal decomposition:

$$C_2H_5OH \rightarrow C_2H_4 + OH$$ \hspace{1cm} (2)

When ethanol is oxidized, oxygen atoms are introduced between the carbon and hydrogen atoms to form molecules containing the OH group. This phenomenon accelerates the processes of oxidation of soot nuclei and prevents coagulation. The following reaction directions are likely:

$$C_2H_5OH + H \rightarrow C_2H_4 + H_2O$$ \hspace{1cm} (3)

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$ \hspace{1cm} (4)

$$C_2H_5 \rightarrow CH_3 + CH_2$$ \hspace{1cm} (5)

$$C_2H_5OH + O \rightarrow C_2H_5O + OH$$ \hspace{1cm} (6)

$$C_2H_5O \rightarrow CH_3O + CH_2$$ \hspace{1cm} (7)

Further, oxidation proceeds through a sequence of reactions for the formation of intermediate products that transfer the reacting system from the initial state to the final products. Such intermediate products can be peroxides, molecules and their fragments with the OH group, hydrogen and oxygen atoms, free radicals [19-23].

Then, from the radicals CH$_3$, CH$_2$, CH$_3$O, atomic carbon C is formed by sequential dehydrogenation:

$$CH_3 \rightarrow -H \rightarrow CH_2 \rightarrow -H \rightarrow CH \rightarrow -H \rightarrow C$$ \hspace{1cm} (8)

$$CH_3O \rightarrow -H \rightarrow CH_2O \rightarrow -H \rightarrow CHO \rightarrow -H \rightarrow C$$ \hspace{1cm} (9)

The CH$_3$ and OH radicals can react with an ethanol molecule:

$$C_2H_5OH + CH_3 \rightarrow 2CH_4 + CHO$$ \hspace{1cm} (10)

$$C_2H_5OH + OH \rightarrow C_2H_4O + H_2O$$ \hspace{1cm} (11)

In addition, OH radicals also participate in reactions with hydrocarbon radicals, as a result of which a water molecule is formed:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$ \hspace{1cm} (12)

$$C_2H_5 + OH \rightarrow C_2H_4 + H_2O$$ \hspace{1cm} (13)

At the next stage, as a result of intermediate reactions, thermal decomposition of hydrocarbons occurs with the formation of acetylene C$_2$H$_2$:

$$C_2H_4 \rightarrow C_2H_2 + H_2$$ \hspace{1cm} (14)
\[ \text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{H} \]  

(15)

Then, thermal decomposition of acetylene occurs, which leads to the formation of C\(_3\)H nucleus radicals. These radicals can subsequently be oxidized to form atomic carbon and water:

\[ \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H} \]  

(16)

\[ \text{C}_3\text{H} + \text{OH} \rightarrow 2\text{C} + \text{H}_2\text{O} \]  

(17)

Further, water molecules formed as a result of chemical reactions and water introduced into the cylinder together with the fuel participate in the oxidation of soot particles. Hydrogen H\(_2\) molecules formed during the reactions can inhibit the surface growth of carbon particles. Inhibition is explained by the active adsorption of H\(_2\) molecules, which prevents the surface from contacting hydrocarbon molecules.

After the formation of physical nuclei, coagulation of primary soot particles occurs, accompanied by a heterogeneous process of surface growth of particles to characteristic sizes of 10 ... 30 nm. The vast majority of the mass of soot particles (> 95%) is formed due to surface growth, and not due to the process of nucleation. The coagulation process consists in the collision of two particles, which then "stick together" with each other with the formation of a common outer shell. The chemistry of the particle growth process is the decomposition of hydrocarbon molecules and radicals on the particle surface. With rapid cooling, part of the high molecular weight hydrocarbons formed during the decomposition of DF molecules do not have time to go through all stages of transformations and are absorbed by the surface of soot particles, which determines the carcinogenic danger of soot.

When working on EFE, the probability of the formation of soot particles from ethanol is relatively small, which is associated with the peculiarities of the combustion of emulsified fuels. The increased efficiency of the combustion process of the emulsion is due to the "microexplosion" of its droplets due to the difference in the boiling points of ethanol and diesel fuel. With additional crushing of the droplets of the emulsion, the rate of their evaporation increases and the mixing of the fuel with air improves, while the combustion process is significantly intensified. As a result, the predominant oxidation of carbon black complexes occurs [24-27].

Simultaneously with the formation of soot particles, they burn out. In the general case, carbon burning is a complex multistage non-stationary heterogeneous reaction process on the outer and inner surfaces of an inhomogeneous carbon particle, determined by both the kinetics of chemical reactions and the counter diffusion of the oxidizing agent and reaction products. The process of burning soot particles leads to a decrease in their size and mass yield as a whole.

Soot burning during the burning of hydrocarbon fuels is considered to be a set of processes for its gasification due to interaction with carbon dioxide and water vapor and oxidation due to a chemical reaction with free oxygen. It is advisable to consider all three reagents as oxidizing agents, and soot as fuel.

The rate of burning of soot particles is determined by the supply of the oxidizing agent due to its laminar or turbulent diffusion to the surface of the particle, as well as the rate of the chemical reaction of oxidation or gasification. In accordance with the rates of these two processes, the total rate of soot particle burn up is established at a certain level of oxidizer concentration on its surface. Particle combustion, depending on the properties of their environment, is determined either by the combined influence of the oxidant diffusion to the particle surface and the kinetics of the chemical reaction on the particle surface, or one of these factors: diffusion or kinetics. For small particle sizes characteristic of soot, the burn-up rate depends, first of all, on the rates of chemical reactions. It was established that the rate of soot oxidation (reaction with oxygen) is several orders of magnitude higher than the rate of gasification reactions. Therefore, if there are all three oxidizing agents in the surrounding gas environment, the main role in soot burnout is played by chemical interaction with oxygen, and in the absence of free oxygen (combustion of rich hydrocarbon-air mixtures), gasification reactions become decisive.
Reactions of carbon with oxygen:

\[ C + O_2 \rightarrow CO_2 \]  \hspace{1cm} (18)

\[ 2C + O_2 \rightarrow 2CO \]  \hspace{1cm} (19)

These two reactions are called primary during the combustion of carbon. At the surface of a burning carbon particle, the interaction of the formed carbon monoxide with oxygen diffusing from the volume is possible:

\[ 2CO + O_2 \rightarrow 2CO_2 \]  \hspace{1cm} (20)

Reactions with water vapor:

\[ C + 2H_2O \rightarrow CO_2 + 2H_2 \]  \hspace{1cm} (21)

\[ C + H_2O \rightarrow CO + H_2 \]  \hspace{1cm} (22)

Interaction with carbon dioxide:

\[ C + CO_2 \rightarrow 2CO \]  \hspace{1cm} (23)

When working on EFE, the reaction with water vapor plays a significant role in the oxidation of soot particles. This is due to the fact that water is one of the components of the emulsion and is formed as a result of chemical reactions during the decomposition of alcohol molecules [28-30].

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