The formation of soot in the cylinder of a diesel engine when operating on methanol-containing motor fuel

A I Chuprakov, A A Anfilatov and A N Chuvashov
Department of thermal engines, Vehicles and tractors, Vyatka State Agricultural Academy, 610017, Kirov, October prospect, 133, Russian Federation

E-mail: chaidvs@mail.ru

Abstract. The chemistry of the formation of soot particles in a cylinder of a diesel engine when working on alternative motor fuel in the form of an emulsion containing methanol alcohol is considered. One of the most dangerous toxic components of liquid fuel combustion products is soot. Therefore, it is necessary to find ways to reduce its content. To do this, you need to know the methods and stages of soot formation, which affect the final concentration by weight. The most important task can be called the determination of the prevailing mechanisms of the appearance of soot in the combustion of liquid fuels in the cylinders of engines. A variable zonal model of soot formation in a 4 H 11.0 / 12.5 high-speed diesel engine is presented when working on an alternative emulsified alcohol fuel - methanol-fuel emulsion. The stages of the formation of carbon particles during the oxidation of fuel inside the cylinder are considered.

The proposed chemical process of soot formation and burning in the cylinder of a diesel engine when operating on alternative motor fuel (alcohol-containing emulsion) is shown in figure 1.

The effect of alcohol fuel on combustion, the formation and oxidation of toxic substances is associated with a local decrease in temperature during the evaporation of most of the methanol, which is injected into the combustion chamber. There is also a possible connection with its temperature conversion and the production of a large number of active radicals CH3 and OH, which contribute to combustion processes, which leads to an improvement in the dynamics of heat generation and can lead to an increase in the maximum temperature of the combustion process.

The low cetane number of methanol lowers the local temperature during evaporation and leads to a shift to the right of TDC of the maximum temperature in the cylinder of a diesel engine when operating on emulsified fuel. This is confirmed experimentally.

After ignition of a drop of an alcohol-containing emulsion prior to its “microexplosion”, there is a certain time delay, this is explained by the need to heat the inner regions of the drop, which is needed to start nucleation of the vapor phase.

The heating rate necessary for boiling methyl alcohol inside an emulsion drop depends on the physical properties of the alcohol-containing fuel.

We assume that there are two main mechanisms that have the greatest impact on the formation of soot particles in the cylinder of a diesel engine. They 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.

When emulsified fuel is injected into the combustion chamber of a diesel engine, fuel hydrocarbons, under the influence of high temperatures, form free radicals.
At temperatures less than 1500 K, the formation of phenyl (C₆H₅) and benzyl (C₄H₃) radicals occurs through a chain of reactions following one after another, which result in the formation of intermediate active substances from both traditional fuel and methyl alcohol. These radicals, when interacting with acetylene (C₂H₂), the C₂H radical, and fuel hydrocarbons, increase the carbon fraction in the hydrocarbon molecule, thereby forming a chemical nucleus of soot particles.

At temperatures above 1500 K, the molecules of methyl alcohol and diesel fuel (DF) are decomposed to form the radicals CH₄, CH₃, CH₂, CH, and atomic carbon. Acetylene and C₂H react with radicals, and a chemical nucleus of a carbon black particle appears, and then in the process of surface growth a physical nucleus of a carbon black particle is created [1-25].

First, we consider the process of soot formation during combustion of diesel fuel.

According to the scheme of soot formation, which was proposed by Professor Tesner P A, a chemical nucleus of a soot particle is formed in the first stage. This transformation leads to a physical nucleus of a soot particle, and a phase transition from a gaseous state to a solid particle occurs.

At the first stage of soot formation from diesel fuel, it occurs according to the radical-chain mechanism proposed by academician N.N. Semenov:

\[ C_{12}H_{30} \rightarrow CH_4 + 3.5C_2H_4 + 2C_3H_6. \] (1)
At the second stage of soot formation from traditional fuels, thermal decomposition and conversion of the resulting hydrocarbons with the formation of acetylene occurs:

\[ \text{C}_2\text{H}_4 + 2\text{H}_2 \rightarrow 2\text{CH}_2; \]  
\[ \text{CH}_4 \rightarrow 0,5\text{C}_2\text{H}_4 + \text{H}_2; \]  
\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + 0,5\text{C}_2\text{H}_2 + 0,5\text{H}_2; \]  
\[ \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2. \]  

At the third stage of the process of soot formation from diesel fuel, there is a thermal explosive decomposition, leading to the formation of radical nuclei of soot particles C₂H:

\[ \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H} + \text{H}; \]  
\[ \text{C}_2\text{H}_2 + 2\text{H} \rightarrow \text{C}_2\text{H}_4; \]  
or

\[ \text{C}_3\text{H}_2 + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} + \text{C}_3\text{H}_3. \]  

The mono radicals C₂H and H formed, when interacting with acetylene molecules, form a benzyl radical:

\[ \text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_3 \]  

At the fourth stage of soot formation from a traditional diesel crowd, the number of carbon atoms in the molecule increases to 100 and the physical surface of the soot particle is formed, i.e. the formation of a physical nucleus of a soot particle occurs:

\[ \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_3 + \text{H}_2; \]  
\[ \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_3 + \text{H}_2; \]  
\[ \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_8\text{H}_3 + \text{H}_2; \]  
\[ \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_5; \]  
\[ \text{C}_6\text{H}_3 \rightarrow \text{C}_6\text{H}_2 + \text{H}; \]  
\[ \text{C}_8\text{H}_3 \rightarrow \text{C}_8\text{H}_2 + \text{H}; \]  
\[ \text{C}_6\text{H}_3 \rightarrow \text{C}_6\text{H}_2 + \text{H}. \]  

Consider the proposed mechanism of soot formation from methyl alcohol.

Hydrogen molecules that are formed during reactions lead to a decrease in the surface growth of carbon particles, then the inhibition can be explained by the active accumulation of hydrogen molecules, which prevent the interaction of the surface with hydrocarbon molecules, as well as the influence of reverse cracking reactions.

At this stage, it should be noted that hydrogen at high temperatures is indeed capable of chemisorptions with a carbon surface, and at higher temperatures it detaches carbon atoms from the surface to form methane and ethane.

It can be assumed that the decomposition of the methyl alcohol molecule at the initial stage will take place in four most probable directions:

\[ \text{CH}_3\text{OH} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{OH}; \]  
\[ \text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_3 + \text{H}_2\text{O}; \]  
\[ \text{CH}_3\text{OH} + \text{O} \rightarrow \text{CH}_2\text{O} + \text{OH}; \]  
\[ \text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}. \]  

At the same time, O₂ atoms are introduced between carbon and hydrogen atoms with the formation of molecules that contain a hydroxyl group and accelerate oxidative processes. Further, oxidation passes
through successive formation reactions with the formation of intermediate products. In addition, OH radicals participate in reactions with products of the primary decomposition of hydrocarbon molecules that make up methyl alcohol and DF, resulting in the formation of an H₂O molecule:

\[
2\text{CH}_4 + \text{OH} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2\text{O} + 2\text{H};
\]

\[
\text{C}_2\text{H}_5 + \text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}.
\]

The second stage of the process of formation of soot particles from methyl alcohol involves the further decomposition of the products of the primary decomposition of methyl alcohol and the formation of new active centers:

\[
\text{CH}_3\text{OH} + \text{CH}_3 \rightarrow \text{CH}_2\text{O} + \text{CH}_4;
\]

\[
\text{CH}_3\text{O} + \text{H} + \text{OH} \rightarrow \text{CH}_3 + \text{HO}_2.
\]

At the third stage, as a result of intermediate reactions, the temperature decomposition of hydrocarbons occurs with the formation of acetylene:

\[
\text{CH}_3 \rightarrow \text{CH}_2 + \text{H};
\]

\[
\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_2 + 3\text{H}.
\]

At the fourth stage of the process of soot formation from methyl alcohol, the temperature decomposition of acetylene occurs and leads to the formation of nucleus radicals, which are subsequently oxidized to form atomic carbon and water:

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

\[
\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_2 + 3\text{H}.
\]

Then, H₂O molecules, which are formed as a result of chemical transformations, and water, which enters the engine cylinder together with fuel, participate in the oxidation of soot particles in expression (29).

After the formation of a physical nucleus, a heterogeneous process of surface growth of a soot particle to a characteristic size occurs. The chemical process of particle growth is the splitting of hydrocarbon molecules or radicals on the surface of a particle. With rapid cooling, part of the high molecular weight hydrocarbons does not have time to go through all the stages of the process and is adsorbed on the surface of soot particles, thereby determining the carcinogenic danger of soot [26-53].

The formation of crystallites can occur during the interaction of radicals, which are combined into single aggregates during coagulation. The particle size will depend on the residence time, the degree of saturation of the system with nuclei.

Coagulation of particles occurs in conjunction with surface growth and significantly affects their shape and structure. The larger the size of the soot particles, the lower their concentration and radical properties. Coagulation is characteristic of particles up to 10 nm in size and is a physical process of interconnecting parts under the action of polarized forces, which, in turn, are the result of the pronounced radical properties of young soot.

Together with the formation of soot, it burns out. The process of soot burning can be considered as gasification, since there is an interaction with carbon dioxide and water vapor, as well as a chemical reaction with oxygen.

The interaction of carbon with an oxidizing agent proceeds with the participation of intermediate formations, which are unstable and for some time are in an adsorbed state on the outer surface of the carbon and on the surface of the pores [54-65].

We can consider the mechanism of chemical and diffusion interaction of a carbon particle with an oxidizing agent. In general, carbon oxidation occurs due to three re-actions:

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO}_2;
\]
\[
\begin{align*}
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2; \\
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2.
\end{align*}
\] (29) (30)

With a sufficiently long reaction time of soot with water vapor and carbon dioxide, gasification reactions will lead to the disappearance of C. Reaction (29) plays a more significant role, since water is one of the components of the emulsion and its concentration in the combustion zone is high. Thus, the presence of soot in the combustion products is associated with the incompleteness of its gasification processes with water vapor and carbon dioxide due to the relatively low rates of their occurrence and lack of residence time.

References
[1] Likhanov V A and Lopatin O P 2018 IOP Conf. Series: Materials Science and Engineering 457 012011
[2] Romanyuk V, Likhanov V A and Lopatin O P 2018 Theoretical and Applied Ecology 3 27-32
[3] Lopatin O P 2020 IOP Conf. Series: Materials Science and Engineering 862 062087
[4] Anfilatov A A and Chuvashov A N 2020 IOP Conf. Series: Materials Science and Engineering 862 062064
[5] Marchuk A, Likhanov V A and Lopatin O P 2019 Theoretical and Applied Ecology 3 080-6
[6] Anfilatov A A and Chuvashov A N 2020 Journal of Physics: Conf. Series 1515 022035
[7] Likhanov V A and Lopatin O P 2019 Journal of Physics: Conf. Series 1399 055016
[8] Skryabin M L and Likhanov V A 2020 IOP Conf. Series: Materials Science and Engineering 734 012075
[9] Likhanov V A and Lopatin O P 2019 Journal of Physics: Conf. Series 1399 055020
[10] Chuvashov A N and Chuprakov A I 2019 Journal of Physics: Conf. Series 1399 055085
[11] Likhanov V A and Rossokhin A V 2020 IOP Conf. Series: Materials Science and Engineering 862 062046
[12] Likhanov V A, Lopatin O P and Yurlov A S 2019 Journal of Physics: Conf. Series 1399 055026
[13] Anfilatov A A and Chuvashov A N 2020 Journal of Physics: Conf. Series 1515 042048
[14] Likhanov V A and Lopatin O P 2020 IOP Conf. Series: Earth and Environmental Science 421 072018
[15] Anfilatov A A and Chuvashov A N 2020 IOP Conf. Series: Materials Science and Engineering 862 062069
[16] Anfilatov A A 2020 Journal of Physics: Conf. Series 1515 042049
[17] Lopatin O P 2020 IOP Conf. Series: Earth and Environmental Science 421 072019
[18] Likhanov V A, Kozlov A N and Araslanov M I 2020 IOP Conf. Series: Materials Science and Engineering 734 012211
[19] Likhanov V A and Rossokhin A V 2020 IOP Conf. Series: Materials Science and Engineering 862 062047
[20] Likhanov V A and Lopatin O P 2017 Thermal Engineering 64(12) 935-44
[21] Skryabin M L 2020 IOP Conf. Series: Earth and Environmental Science 421 072012
[22] Lopatin O P 2020 Journal of Physics: Conf. Series 1515 042021
[23] Chuvashov A N and Chuprakov A I 2020 IOP Conf. Series: Materials Science and Engineering 862 062089
[24] Likhanov V A and Lopatin O P 2020 Journal of Physics: Conf. Series 1515 052002
[25] Likhanov V A and Lopatin O P 2020 IOP Conf. Series: Materials Science and Engineering 862 062014
[26] Kopchikov V N and Fominynkh A V 2020 Journal of Physics: Conf. Series 1515 042028
[27] Likhanov V A and Anfilatov A A 2020 IOP Conf. Series: Materials Science and Engineering 862 032048
[28] Anfilatov A A and Chuvashov A N 2020 Journal of Physics: Conf. Series 1515 042052
[29] Lopatin O P 2020 Journal of Physics: Conf. Series 1515 042009
[30] Devetyarov R R and Chuvashev A N 2020 Journal of Physics: Conf. Series 1515 042080
[31] Likhanov V A and Lopatin O P 2019 Ecology and Industry of Russia 23(9) 60-5
[32] Chuvashev A N, Chuprakov A I and Anfilatov A A 2020 IOP Conf. Series: Materials Science and Engineering 734 012184
[33] Likhanov V A and Rossokhin A V 2020 IOP Conf. Series: Materials Science and Engineering 734 012207
[34] Likhanov V A and Lopatin O P 2020 Journal of Physics: Conf. Series 1515 042008
[35] Lopatin O P 2020 Journal of Physics: Conf. Series 1515 052004
[36] Chuvashev A N and Chuprakov A I 2020 IOP Conf. Series: Materials Science and Engineering 862 062083
[37] Likhanov V A and Lopatin O P 2020 Journal of Physics: Conf. Series 1515 042019
[38] Skryabin M L and Likhanov V A 2019 Journal of Physics: Conference Series 1399 044063
[39] Likhanov V A and Anfilatov A A 2020 IOP Conf. Series: Materials Science and Engineering 862 032050
[40] Skryabin M L 2020 Journal of Physics: Conf. Series 1515 042107
[41] Likhanov V A and Anfilatov A A 2020 IOP Conf. Series: Materials Science and Engineering 862 032044
[42] Likhanov V A and Lopatin O P 2018 Ecology and Industry of Russia 22(10) 54-9
[43] Likhanov V A and Rossokhin A V 2018 IOP Conf. Series: Materials Science and Engineering 457 012007
[44] Likhanov V A and Skryabin M L 2019 IOP Conf. Series: Earth and Environmental Science 315 032045
[45] Likhanov V A and Rossokhin A V 2019 Journal of Physics: Conf. Series 1399 044038
[46] Likhanov V A and Lopatin O P 2020 IOP Conf. Series: Materials Science and Engineering 734 012202
[47] Likhanov V A, Lopatin O P and Yurlov A S 2020 IOP Conf. Series: Materials Science and Engineering 734 012208
[48] Lopatin O P 2020 IOP Conf. Series: Materials Science and Engineering 734 012199
[49] Kozlov A N, Anfilatov A A and Chuvashev A N 2019 Journal of Physics: Conf. Series 1399 055051
[50] Rossokhin A V and Anfilatov A A 2020 IOP Conf. Series: Materials Science and Engineering 862 062065
[51] Anfilatov A A and Chuvashev A N 2020 Journal of Physics: Conf. Series 1515 042077
[52] Anfilatov A A 2020 Journal of Physics: Conf. Series 1515 042098
[53] Likhanov V A, Lopatin O P and Vylegzhanin P N 2020 IOP Conf. Series: Materials Science and Engineering 862 062074
[54] Chuvashev A N and Chuprakov A I 2020 Journal of Physics: Conf. Series 1515 042094
[55] Likhanov V A, Kopchikov V N and Fominykh A V 2020 Journal of Physics: Conf. Series 1515 042026
[56] Anfilatov A A and Chuvashev A N 2020 IOP Conf. Series: Materials Science and Engineering 862 032052
[57] Likhanov V A, Rossokhin A V and Devetyarov R R 2020 Journal of Physics: Conf. Series 1515 042064
[58] Skryabin M L and Grebnev A V 2020 Journal of Physics: Conf. Series 1515 052052
[59] Likhanov V A and Lopatin O P 2020 IOP Conf. Series: Materials Science and Engineering 862 062027
[60] Skryabin M L 2020 Journal of Physics: Conf. Series 1515 04283
[61] Likhanov V A and Lopatin O P 2020 IOP Conf. Series: Materials Science and Engineering 862 062033
[62] Likhanov V A, Lopatin O P and Vylegzhanin P N 2020 IOP Conf. Series: Materials Science and Engineering 862 062078
[63] Lopatin O P 2020 *IOP Conf. Series: Materials Science and Engineering* **862** 062025
[64] Anfilatov A A and Chuvashev A N 2020 *IOP Conf. Series: Materials Science and Engineering* **862** 032055
[65] Devetyarov R R 2020 *IOP Conf. Series: Materials Science and Engineering* **862** 062072