Simulation of soot formation in a tractor diesel engine running on rapeseed oil methyl ether and methanol

V A Likhanov, O P Lopatin¹, A S Yurlov and N S Anfilatova
Department of thermal engines, automobiles and tractors, Vyatka State Agrotechnological University, October prospect, 133, 610017, Kirov, Russian Federation

¹E-mail: nirs_vsaa@mail.ru

Abstract. The mass content of soot (C) in the cylinder of a tractor diesel engine (TDE) is directly affected by the temperature conditions, the excess air coefficient, and the chemical composition of the fuel. Methanol (M) does not form C particles during combustion. As the C chain in the fuel molecule increases, the propensity to C formation during combustion increases. However, in the presence of oxygen atoms in the initial fuel molecule, it significantly slows down the rate of nucleation of primary particles. During the evolution of the particle in the cylinder of a TDE when working on rapeseed oil methyl ether and methanol (ROMEM), a number of characteristic stages are identified.

The countries of South America (Brazil, Argentina) and Asia (Japan) are the first to use alcohol fuels in TDE. In European countries, the use of M is of particular interest.

M ranks second after ammonia in terms of production (4 million tons) in the Russian gas chemical industry. M is a fundamental raw material in the chemical industry, a large share of which is accounted for in the production of synthetic resins. The second most important industry, consuming more than 20% of M, is octane-enhancing substances (fuel additives), a significant share of which is methyl tert-butyl ether. The main producers of MTBE include the production associations Omsk Rubber, Uralorgsintez, EKTOS-Volga, SIBUR Tobolsk, NKNH, etc. At the moment, Russian oil refineries consume about 80% of all methyl tert-butyl ether produced in the country, the rest is exported. Among the largest producers of M are: JSC Metafrax (Perm region), JSC Tolyattiazot (Samara region), JSC Shchekinoazot, JSC NAC Azot (Tula region), JSC Nevinnomyssky Azot (Stavropol region), JSC Ammonium (Tatarstan) [1-6].

The use of M in TDE makes it possible to effectively reduce the C content in them. Figure 1 shows images of C particle agglomerates taken using high-resolution transmission electron microscopy, which show more or less branched aggregates, and each agglomerate consists of tens to hundreds of spherical or almost spherical primary particles.

In addition, most of the primary particles partially overlap with their neighboring primary particles during the fusion of the soot nuclei. To accurately analyze the microstructure of aggregate particles, the primary particle size $d_p$ and the fractal dimension $D_f$ are determined.

The primary particle size $d_p$ is the average primary diameter that can be visually determined by transmission electron microscopy of sample images. The fractal dimension is a useful parameter for describing the structure of agglomerates and the mechanism of agglomeration. Generally, a higher $D_f$...
value represents a more spherical structure, while a lower $D_f$ value means a less compact and more branched morphology [7-11].

Figure 1. C agglomerates: a - images of selected primary C agglomerates; b - primary $d_p$ scheme.

Figure 2 shows the carbon black on the nanoscale: the inner core and the outer shell. The inner core contains several small particles with the core covered with carbon layers of a turbostratic structure. In contrast, the outer shell consists of graphite crystallites oriented parallel to the outer surface.

Figure 2. Typical shell-core structure of a primary C particle.

This is confirmed by the results of transmission electron microscopy (figure 3). High-magnification transmission electron microscopy micrographs also show the previously described bulbous subunits that are incorporated into the primary particles [12-19]. They have an average size of about 5 nm and are not easy to distinguish on raw scattering curves, since such small particles will only be scattered at $q \sim 0.1 \text{ Å}^{-1}$.

The C C$_{12}$–C$_{20}$ particles deposited on the active branched surface can be millions of times more dangerous than carbon monoxide. It is known that droplets with different energies and geometric characteristics collide with hot air, break up, warm up and intensively evaporate [20-27].
Figure 3. Transmission electron microscopy - micrographs of C particles: a - agglomerate; b - primary particle.

Assuming that the fuel torch consists of an array of droplets with an average Sauter diameter, it is possible to determine with acceptable accuracy, based on Sreznevsky’s law, the fraction of fuel that has evaporated by the moment $\varphi_i$:

$$\sigma_u = \sum_{i=1}^{j} \frac{d\sigma_i}{d\sigma_0} \left( d_0^2 - K \frac{\varphi - \varphi_i}{6n} \right)^{\frac{3}{2}},$$

(1)

where $\sigma_u$ – percentage of fuel vaporized; $j$ – number of calculation steps; $i$ - calculation step; $K$ – the evaporation constant.

After evaporation, the ROMEM molecules disintegrate during the transition to the pre-flame zone to form new C of lower molecular weight [34-39].

To account for the oxidation process of fuel decomposition products, we consider reversible reactions:

$$C_2H_2 + O_2 \rightarrow 2CO + H_2; \ H_2 + 0.5 \ O_2 \rightarrow H_2O; \ CO + 0.5 \ O_2 \rightarrow CO_2; \ CO + H_2O \rightarrow CO_2 + H_2;$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2; \ CH_4 + CH_4 \rightarrow C_2H_2 + 3H_2; \ C_2H_2 + 3H_2 \rightarrow CH_4 + CH_4.$$

Thus, in the pre-flame zone, in addition to acetylene and oxidation products, a certain amount of methane, propylene, ethylene and other products of high-temperature pyrolysis will be contained [34-39]. The differential equation for determining the CN of pyrolysis products and initial C in the pre-flame zone can be written:

$$\frac{dM_i}{d\varphi} = \left( \frac{dM_i}{d\varphi} \right)_\sigma + \left( \frac{dM_i}{d\varphi} \right)_k + \left( \frac{dM_i}{d\varphi} \right)_x.$$

(2)

The change in the CN of vaporized ROMEM in the reaction zone can be determined by the expression:
\[
\frac{dM_i}{d\phi} = \frac{\mu_i}{V_p^2} \left( \frac{d\sigma_{ui}}{d\phi} V_p - \frac{dV_p}{d\phi} \cdot d\sigma_{ui} \right), \quad i = 1, 2, \tag{3}
\]

where \(\mu_i\) - calculated cyclic number of moles of the i-th gas, \(V_p\) – reaction zone volume.

The size of the reaction zone:

\[
V_p = 83.14 \Sigma R_i T_i / P,
\tag{4}
\]

where \(R_i\) - the number of moles of the i-th gas component per kg of the main fuel, mol; \(P\) - cylinder pressure indicator, MPa.

Particle CN transition rate:

\[
\frac{dM_i}{d\phi} = M_i \frac{d\chi}{d\sigma_{ui} - \chi},
\tag{5}
\]

where \(\chi\) – integral law of heat dissipation.

Although C is generally electrically neutral, it contains a relatively large proportion of the charged particles found in the flame. The distributed electric charge promotes an increase in the rate of coagulation in the oxidation zone. It is established that the process continues in the exhaust system [40-46]. The speed of the process under consideration depends on the particle CN, pressure, and temperature conditions. The speed of the Brownian coagulation process is determined by the expression:

\[
\frac{dN_p}{dt} = -k_{coag} N_p^2,
\tag{6}
\]

where \(k_{coag}\) - coagulation constant; \(N_p\) - piece CN of C particles.

Then equation (6) can be written as:

\[
\frac{dN_p}{d\phi} = \frac{dN_{ed}}{d\phi} - P_0 C_{coag} (DT)^{1/2} N_p^2,
\tag{7}
\]

where \(P_0\) - steric factor; \(C_{coag}\) - constant coefficient of coagulation rate.

Let's denote \(G\) - the mass of C in the zone. Then the mass of C:

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

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

\[
\frac{dm_p}{m_p} = \frac{dG}{G} - \frac{dN_p}{N_p},
\tag{8}
\]

We determine the rate of change in the particle diameter during coagulation. As a result of this process, the total mass of C in the corresponding zone does not change. Expression (8) can be written:

\[
\frac{dm_p}{d\phi m_p} = -\frac{dN_p}{d\phi N_p}.
\tag{9}
\]

We get the rate of change in the C diameter during coagulation:
\[ \frac{dD_{\text{coag}}}{d\varphi} = -\frac{1}{3} m_p^3 \frac{1}{d\varphi N_p} \cdot \frac{dN_p}{d\varphi}. \]  

(10)

Change in C diameter during coagulation:

\[ \frac{dD_{\text{coag}}}{d\varphi} = -\frac{1}{3} m_p^3 P_0 C_{\text{coag}} (D T)^{\frac{1}{3}} N_p, \]

(11)

where \( m_p \) - particle mass; \( P_0 \) - steric factor; \( C_{\text{coag}} \) - constant coefficient of coagulation rate; \( D \) - particle diameter; \( N_p \) - piece CN of C particles.

Oxidation reactions take place on the surface and the boundary volume:

\[ C + O_2 \rightarrow CO_2; \quad C + 0.5O_2 \rightarrow CO; \quad C + CO_2 \rightarrow 2CO; \]
\[ C + 2H_2O \rightarrow CO + 2H_2; \quad 2CO + O_2 \rightarrow 2CO_2; \quad 2H_2 + O_2 \rightarrow 2H_2O. \]

The main oxidizing agents of C in the TDE running on ROMEM are oxygen, water, hydroxide group radicals.

OH radicals:

\[ CO_2 + H \rightarrow CO + OH; \quad O_2 + 2H \rightarrow 2OH. \]

In turbulent combustion, the C particles are located inside the turbulent swirls. The reactions depend on the dissipation of turbulent vortices of unburned gas, mixing of C particles, and small-scale turbulent vortices [47-52]. Moreover, oxygenated groups, such as carboxyl, lactone, and carbonyl groups, may provide a different pathway for oxidation reactions [53-57]. For example, the specific rate of C gasification (C flow) is usually expressed as:

\[ J_c = 12 \cdot 10^3 K_{O_2} C_{O_2}, \]

where \( K_{O_2} \) - rate constant of the oxidation reaction; \( C_{O_2} \) - molar oxygen CN; \( J_c \) - carbon flux, g/m²s.

Then the rate of burnout of C particles can be expressed:

\[ R_{C+O_2 \rightarrow CO} = J_c F, \]

where \( F \) - total particle surface.

The cross section of the collision of a C particle with an oxygen molecule can be represented as the cross-sectional area of a C particle in diameter:

\[ \sigma = \frac{\pi D^2}{4}. \]

Then the reaction rate can be written

\[ R_{C+O_2 \rightarrow CO} = 9.4 \cdot 10^3 K_{O_2} C_{O_2} D^2 N. \]

Thus, the modeling of soot content in a TDE based on ROMEM should combine descriptions of many physical and chemical phenomena.

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