The impact of the use of compressed natural gas in a car diesel engine on the formation and oxidation of soot particles

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Abstract. The problems of using compressed natural gas in diesel as an alternative fuel and reducing the content of harmful substances in exhaust gases are considered. At the same time, the problems of formation and burning of soot particles in the diesel cylinder during its operation on natural gas and their influence on the combustion process and flame characteristics are considered separately. The results of bench tests on the impact of the use of compressed natural gas on the effective performance, environmental performance and fluidity of exhaust gases are presented. The parameters of the combustion process and heat dissipation characteristics are considered, the values of the mass content of soot in the engine cylinder depending on the angle of rotation of the crankshaft are calculated. The optimal values of the effective parameters, characteristics of the combustion process, toxicity and smokiness of exhaust gases during the operation of diesel on compressed natural gas are determined.

Conversion of the considered diesel from oil diesel fuel to compressed natural gas allowed to reduce the content of nitrogen oxides in the exhaust gases by 17.0%, soot in 25 times, carbon dioxide by 10.1%.

1. Introduction
The intensity of fuel combustion, which determines the nature and dynamics of heat release, depends on the physical and chemical processes occurring in the reaction zone. And the conditions under which these reactions occur, especially in engines with internal mixing, undoubtedly, are clearly dependent on the location of the local volume of the combustion chamber under consideration.

Another interesting, important, but little-studied process is the process of radiation heat exchange in the combustion chamber of diesel. The complexity of the study of this phenomenon is due to the presence in the combustion chamber of diesel a large number of soot particles of different shapes and sizes, the emissivity of which significantly exceeds the emissivity of gases, and the processes of formation and, accordingly, the burning of these particles have a clearly expressed local character. And to calculate the processes of formation and burnout of soot, relying solely on the indicator diagram is possible only as a first approximation [1].

For the combustion chambers of diesel engines in the calculation of radiation heat transfer is required to take into account the list of features of the working process associated with the cyclicity and instability of the working process and with the geometric parameters of the combustion chamber and the fuel torch. Depending on the intensity of the turbulence of the air charge in the combustion chamber and the parameters of the fuel jet injected by the nozzle, a volume of gases containing soot particles is formed. The presence of a certain duration of fuel supply, different size of dt droplets in the
torch, a lot of random self-ignition points, turbulence of the air charge in the cylinder as a result of the movement of the piston and fuel combustion, the changing volume of the cylinder, the continuously changing number of soot particles and their sizes practically reduce to zero the possibility of direct calculation of the number of soot particles in the local volume and their sizes, which is required for calculations of radiation heat exchange in the combustion chamber [2].

The processes of fuel injection and atomization are studied in detail [3]. Knowing the law of fuel supply, injection pressure, the diameter of atomizing holes, physical and chemical properties of the fuel, the conditions in the combustion chamber can be sufficient for further calculations to determine the size, shape, and process of development of the fuel-air jet. It is well known that the main part of the combustion and heat generation process is completed in 50...60° after TDC. It is during this period that the main amount of fuel in the combustion chamber is burned when the piston is near the TDC, the pressure and temperature of the gases in the engine cylinder reach maximum values, as well as the concentration of soot particles [4]. This, in turn, leads to the fact that the emissivity of the flame is high.

2. Experimental part

The quality of fuel atomization depends on its viscosity, pressure in the CS, geometrical parameters of the sprayer, fuel intensity, etc. At the same time in the volume of the torch will always be fuel droplets that differ in size and fractional composition. And since the dynamics of combustion and soot formation is determined mainly by these parameters, as well as the intensity of the turbulence of the air flow in the CS, reliable data for the calculation of radiant heat transfer can be obtained only on the basis of their experimental determination.

According to the data given in [5], the rate of soot burnout can be estimated, for example, from the fact that the originally formed particles have a certain size, and by the end of the working stroke completely burn out. The particle size found in combustion products in diesel engines can be estimated at (0.2...1.0)×10⁻⁶ m. For an engine with a crankshaft rotational speed of 1500 min⁻¹, the visible burning time is (7...8)×10⁻³ s, i.e. at a linear rate of reduction of the particle radius, the soot burnout rate can be estimated as 2.5×10⁻³ ... 1.25×10⁻⁴ m³ / s. If we assume the density of soot is 2×10³ kg / m³, then the average heat generation rate on the surface of soot will be 850 ... 4300 W / m³. Part of this energy is used to heat the combustion products, the part is transferred to the environment by convection, part – by radiation. The approximate heat capacity of the reaction products is estimated as the sum of the heat capacities of the components, for example, CO₂ and N₂. With the burnout rate adopted above, the heat capacity of the combustion products obtained per unit time per unit of soot surface will be 16.2×10⁵ W / (m² K). In this case, to estimate the intensity of convective heat transfer for the accepted conditions, the heat transfer coefficient α will be 2.5·10⁴...1.25·10⁵ W/(m²·K) [6].

Thus, at the accepted rate of burnout of soot particles, only due to the mechanism of convective heat exchange, all the released energy is released into the environment when the temperature of the soot particle is higher than the ambient temperature by less than 1 K. This makes it possible to further consider combustion products containing soot particles as a homogeneous radiating, absorbing and scattering medium [7].

At the same time, soot particles are located not only in the volume of the cylinder but also in the so-called boundary layer, i.e. the layer adjacent to the walls of the cylinder and CS. The thickness of this layer is 2...3 mm at the end of the expansion stroke [8]. In the work [9] it is noted that the soot particles have a lower temperature near the wall than in the core of the torch. Under these conditions, the combustion of soot particles is slowed down so they can not be any noticeable sources of heat. Based on this, it is concluded that the intensity of convective heat transfer in the engine cylinder is determined by the flow conditions and the state of the gas in the immediate vicinity of the wall, while the intensity of radiant heat transfer depends on the concentration and temperature of the combustion products, including soot particles, in the cylinder volume [10].

To determine the intensity of radiation heat transfer in a medium containing suspended particles, in addition to the boundary conditions, the spectral absorption and scattering coefficients of the particles
and the radiation scattering indicatrix on the particles must also be known \[11\]. These characteristics, in turn, depend on the physical nature of the substance of the particles (the complex refractive index of the material of the particles), their size, concentration, shape, and wavelength of radiation. The most well-known works devoted to the solution of the problem of finding the scattering and absorption indices on various particles include \[12, 13, 14, \text{etc.}].

3. Results
Consider the process of thermal pyrolysis of methane, which is the main component of natural gas, in the cylinder of gas diesel.

Pyrolysis is characterized by simultaneous reactions of thermal decomposition and synthesis of more complex compounds as a result of radical chain chemical reactions \[15\].

At the first stage of the pyrolysis process, the formation of free radicals from the methane molecule occurs as a result of breaking the C – C bond, for example, methylene CH\(_2\) or methyl CH\(_3\). The obtained radicals react with the molecule of the initial hydrocarbon, which supports the chain mechanism \[16\].

\[
\begin{align*}
\text{CH}_4 & \leftrightarrow \text{CH}_2 + \text{H}_2; \\
\text{CH}_2 + \text{CH}_4 & \leftrightarrow \text{C}_2\text{H}_6.
\end{align*}
\]

or

\[
\begin{align*}
\text{CH}_4 & \leftrightarrow \text{CH}_3 + \text{H}; \\
\text{CH}_3 + \text{CH}_4 & \leftrightarrow \text{C}_2\text{H}_6 + \text{H}
\end{align*}
\]

At the second stage, there is a further decomposition of the hydrocarbon molecule

\[
\text{C}_2\text{H}_6 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2
\]

Consider the third stage of the process of pyrolysis of methane:

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

In a direct reaction, acetylene is formed - a compound with a triple carbon bond. The reverse reaction is associated with the rupture of the third carbon bond and the production of a compound with a double carbon bond and two free carbon reducing agents (biradical acetylene).

With a further increase in temperature in the fourth stage of the pyrolysis process, acetylene is subjected to further chemical transformation.

Simultaneously with the decomposition reactions, which are sources of atomic hydrogen and acetylene radical, the synthesis reactions of more complex compounds occur by a radical-chain mechanism according to the well-known theory of chain reactions of academician N. N. Semenova:

\[
\begin{align*}
\text{H} + \text{C}_2\text{H}_2 & \rightarrow \text{C}_2\text{H} + \text{H}_2; \\
\text{C}_2\text{H} + \text{C}_2\text{H}_2 & \rightarrow \text{C}_4\text{H}_2 + \text{H}; \\
\text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 & \rightarrow \text{C}_6\text{H}_2 + \text{H}.
\end{align*}
\]

American scientists in the explosive combustion of acetylene, using mass spectroscopic measurements detected diacetylene (C\(_4\)H\(_2\)), phenylacetylene (C\(_6\)H\(_2\)), C\(_8\)H\(_2\).

Similar to acetylene phenylacetylene C\(_6\)H\(_2\), easily enters the polymerization reaction, can form a polyradical, which is a carbon black embryo.

According to the concept of P. A. Tesner \[17\], the soot molecule is formed as a result of further growth of the soot embryo. In one of the stages of soot formation occurs Benz(\(\alpha\))pyrene. N. V. Lavrov, N. L. Staskevich and G. P. Komina \[18\] proposed the mechanism of formation of Benz(\(\alpha\))pyrene molecules from the soot embryo according to the following scheme.
The General stoichiometric equation of Benz(α)pyrene is as follows:

\[ \text{C}_{20}\text{H}_{12} = \text{C}_6\text{H}_2 + 3\text{C}_2\text{H}_2 + 4\text{C}_2\text{H}. \]  

(10)

With the complication and development of the polycyclic hydrocarbon lattice, a class of compounds called low-temperature soot arises, with a general stoichiometric equation

\[ \text{C}_m\text{H}_n = \text{C}_6\text{H}_2 + 3\text{C}_2\text{H}_2 + \alpha\text{C}_2\text{H} + \beta\text{C}_2. \]  

(11)

It has been established [19] that when natural gas is burned, the content of Benz(α)pyrene in combustion products increases with a decrease in the excess air ratio.

Experimental studies and practice of obtaining soot from liquid fuels, as well as in the process of pyrolysis of coal containing volatile substances, indicate the possibility of obtaining it at low temperatures. When some petroleum hydrocarbons or naphthenic oils were decomposed during pyrolysis, diphenyl was found [20].

In our opinion, diphenyl is the main building block of hydrocarbons with a ringed structure. Diphenyl is formed by the reaction

\[ 2\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5-\text{C}_6\text{H}_5 + \text{H}_2, \]  

(12)

To build molecules of benz(α)pyrene a single biphenyl molecule and two molecules of butadiene. Divinyl is obtained by a radical chain reaction of ethylene

\[ \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_6 + \text{H}, \]  

(13)

and reacts with diphenyl.

\[ 2\text{C}_4\text{H}_6 + \text{C}_6\text{H}_5-\text{C}_6\text{H}_5 \rightarrow \text{C}_{20}\text{H}_{12} + 5\text{H}_2. \]  

(14)

On the other hand, divinyl molecules can undergo rapid reactions of diene synthesis to form aromatic structures:

\[ \text{C}_4\text{H}_6 + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{H}_2. \]  

(15)

It should be noted that the reaction of the synthesis of Benz(α)pyrene with increasing pressure is accelerated.

Consideration of the theoretical foundations of the formation of Benz(α)pyrene reveals methods to help suppress the formation of this harmful substance.

The most fundamental way to destroy Benz(α)pyrene, which is a polycyclic hydrocarbon, is its additional afterburning, as a result of which the total combustion process should take place at \( \alpha \geq 1 \).

Dilution of methane with hydrogen radical-chain reactions of formation of benzo(α)pyrene will be greatly diminished. This is evidenced by thermodynamic calculations and experimental data.

Significant interest is the dependence of the yield of Benz(α)pyrene on the ratio of C/N and N/S in the hydrocarbon molecule. Zero concentration of Benz(α)pyrene will occur, obviously, in the combustion of pure carbon and hydrogen.

The use of compressed natural gas (CNG) as a motor fuel when converting a diesel engine to work on a gas-diesel cycle allows reducing soot emissions from exhaust gases. This achieves a proportional reduction in the emissions of Benz(α)pyrene and improves the environmental performance of ice. That is, the use of CNG is one of the most effective ways to reduce the soot content in the exhaust gas.
Figure 1. Distribution of soot particles by size in the diesel cylinder and the number of soot particles per unit volume \((n = 2400 \text{ min}^{-1} \text{ and } p_e = 0.84 \text{ MPa})\).
assumed 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 takes place 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, it is possible to take into account the supply of matter to the surface of the particle 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 the volume, that is, it is necessary to take into account the supply of matter to the inner surface of the particle.

References

[1] Likhanov V A and Lopatin O P 2018 Ecology and Industry of Russia 22
[2] Sinyavsky V V, Alekseev I V, Ivanov I Y, Bogdanov S N and Trofimenko Y V 2017 Pollution Research 36 686-92
[3] Zhilenkov A A and Efremov A A 2017 IOP Conference Series: Materials Science and Engineering 10 012043
[4] Sinyavsky V V, Shatrov M G, Dunin A Y, Shishlov I G and Vakulenko A V 2019 Periodicals of Engineering and Natural Sciences 7 281-6
[5] Romanyuk V, Likhanov V A and Lopatin O P 2018 Theoretical and Applied Ecology 3
[6] Luksho V A, Kozlov A V, Terenchenko A S and Grinev V N 2018 International Journal of Mechanical Engineering and Technology 9 1385-95
[7] Likhanov V A and Lopatin O P 2017 Thermal Engineering 64
[8] Shatrov M G, Sinyavski V V, Dunin A Y, Shishlov I G, Vakulenko A V and Yakovenko A L 2018 International Journal of Engineering and Technology 7 288-295
[9] Chen W, Pan J, Liu Y, Fan B, Liu H and Otchere P 2019 Applied Energy 176 453-467
[10] Likhanov V A and Lopatin O P 2018 IOP Conference Series: Materials Science and Engineering 457 012011
[11] Gough R V and Bruno T J 2012 Energy and Fuels 26 6905-13
[12] Chai X, Mahajan D and Tonjes D J 2016 Progress in Energy and Combustion Science 56 33-70
[13] Likhanov V A and Lopatin O P 2019 Ecology and Industry of Russia 23
[14] Marchuk A, Likhanov V A and Lopatin O P 2019 Theoretical and Applied Ecology 3
[15] Rajesh Kumar B and Saravanan S 2016 Renewable and Sustainable Energy Reviews 60 84-115
[16] Mikulski M and Wierzbicki S 2016 Journal of Natural Gas Science and Engineering 31 525-37
[17] Likhanov V A and Rossokhin A V 2018 IOP Conference Series: Materials Science and Engineering 457 012007
[18] Lif A and Holmberg K 2006 Advances in Colloid and Interface Science 123 231-39
[19] Aydin F and Ogut H 2017 Renewable Energy 103 688-94
[20] Datta A and Mandal B K 2016 Applied Thermal Engineering 98 670-82
[21] Likhanov V A and Skryabin M L 2019 IOP Conference Series: Earth and Environmental Science 315 032045