Comprehensive analysis of exhaust gas toxicity of heat engines and methods for neutralizing nitrogen oxides

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Abstract. These studies are devoted to assessing the impact of exhaust gases of internal combustion engines on the environment and methods for neutralizing nitrogen oxides. With intensive urbanization and the growth of megacities, road transport has become the most adverse environmental factor in protecting human health and the environment. The formation of toxic substances-products of incomplete combustion of hydrocarbon fuel and compounds of atomic nitrogen with oxygen in the engine cylinder during combustion occurs in fundamentally different ways. Only a comprehensive analysis of this issue will allow us to develop new promising ways to reduce the toxicity of exhaust gases.

1. Introduction
Toxic components make up 0.2...5% of the exhaust gas volume, depending on the type of engine and its operating mode. For a long time, the problem of automobile emissions and air pollution has been developed many methods and methods to reduce the number of exhausts or reduce their toxicity. Currently, measures are being developed and implemented to reduce air pollution from automobile engine emissions, including improving engine designs and improving manufacturing quality.

At the same time, there is a search for new types of fuel, the use of various additives to it, the creation of power plants for cars that emit fewer harmful substances and the development of devices that reduce the content of harmful components in the exhaust gases.

At present, reducing air pollution with toxic substances from road transport is one of the most important problems facing humanity. Air pollution has a harmful effect on people and the environment. The material damage caused by air pollution from road transport is difficult to assess. With intensive urbanization and the growth of megacities, road transport has become the most adverse environmental factor in protecting human health and the environment [1-5].

According to experts, the annual total emissions of vehicles are 400 million tons, including about 27 million tons of carbon oxides (CO), 2.5 million tons of hydrocarbons (CnHm), 9 million tons of compounds of atomic nitrogen with oxygen (NOx), 200...230 million tons of carbon dioxide (CO2). Among all types of transport, road transport causes the greatest damage to the environment. In Russia, about 64 million people live in areas of high air pollution, and the average annual concentrations of air pollutants exceed the maximum allowed in more than 600 Russian cities. The level of air pollution along urban roads in Russia with carbon oxides (CO) reaches 3...5 maximum permissible concentrations, and compounds of atomic nitrogen with oxygen (NOx) 15...25 maximum permissible concentrations. The same tense environmental situation exists in most European countries [6-8].
The main cause of air pollution is incomplete and uneven combustion of hydrocarbon fuels. When a stoichiometric mixture of hydrocarbon fuel and air is completely burned, the combustion products must contain nitrogen (N\(_2\)), carbon dioxide (CO\(_2\)), and water (H\(_2\)O). In real conditions the exhaust gas also contains products of incomplete combustion of fuel: carbon monoxide (CO), aldehydes, solid carbon particles, peroxide compounds, hydrogen (H\(_2\)) and excess oxygen (O\(_2\)), products of thermal reactions of nitrogen-oxygen interaction (NO\(_x\)), as well as inorganic compounds of various substances present in the fuel (sulfur dioxide, lead compounds, and other toxic components) [9-11].

The exhaust gases of internal combustion engines contain about 200 harmful components, of which more than 160 are derivatives of hydrocarbons formed during incomplete combustion of fuel in internal combustion engines. The composition of exhaust gases depends on the type of fuel used, additives and oils, engine operating modes, its technical condition, and vehicle driving conditions. The toxicity of the exhaust gases of gasoline engines is mainly due to the content of carbon oxides, and diesel engines - compounds of atomic nitrogen with oxygen and smoke. Among the harmful components are solid emissions containing soot particles, on the surface of which polycyclic hydrocarbons are adsorbed, which have carcinogenic properties [12-15].

The formation of toxic substances - products of incomplete combustion and compounds of atomic nitrogen with oxygen (NO\(_x\)) in the engine cylinder during combustion occurs in fundamentally different ways. The first group of toxic substances is associated with chemical reactions of fuel oxidation that occur both during the pre-flame period and during the combustion-expansion process. The second group of toxic substances is formed when nitrogen and excess oxygen are combined in the combustion products. The reaction of compounds of atomic nitrogen with oxygen formation is thermal in nature and is not directly related to fuel oxidation reactions (provided that the fuel does not contain chemically bound nitrogen). Therefore, it is advisable to consider the mechanism of formation of these toxic substances separately [16-18].

In general, engine exhaust gases may contain the following non-toxic and toxic components: O, O\(_2\), O\(_3\), C, CO, CO\(_2\), CH\(_4\), C\(_6\)H\(_6\), NO, NO\(_2\), N, N\(_2\), NH\(_3\), HNO\(_3\), HCN, H, H\(_2\), OH, H\(_2\)O. The main toxic substances - products of incomplete combustion are soot, carbon oxides, hydrocarbons, aldehydes and products of the interaction of air nitrogen with oxygen atoms - compounds of atomic nitrogen with oxygen.

Anthropogenic pollution caused by exhaust gases from heat engines affects living organisms, including humans, in a variety of combinations and in a complex way. Their integral influence can only be estimated by the reaction of living organisms or entire communities. The forecast of human exposure to heavy metal-contaminated water, chemical additives in food, or polluted air is valid if the toxicity assessment includes not only analytical methods, but also biological diagnostics of the environment. In addition, many substances that are foreign to the biosphere accumulate in the body, and as a result, prolonged exposure to even small concentrations of these substances causes pathological changes in the body. Also known is the paradoxical effect of small doses of many chemical compounds, when ultra-low doses of toxic components have a stronger effect on the body than their average doses and concentrations.

Various types of anthropogenic impact on the soil can change the conditions for the existence of soil microorganisms, disrupt the normal course of microbial transformation processes in soils and, consequently, affect the processes of transformation of substances in the biosphere. Soil microorganisms participate in cycles of vital elements, such as nitrogen, phosphorus, sulfur, iron, manganese, etc. They have a unique role in cleaning the biosphere from pollution, since it is microorganisms that have a high ability to adapt and can quickly transform pollutants, both natural to the biosphere and foreign.

Practice has shown that it is impossible to achieve the level of toxicity of exhaust gases required by the legislation of developed countries in the first three ways. Therefore, the neutralization of exhaust gases in the exhaust system has become widespread. In this case, the toxic fumes released from the engine cylinders are neutralized before they are released into the atmosphere.

The emission of NO\(_x\) with exhaust gases, according to the classical theory of compounds of atomic nitrogen with oxygen formation, depends on the temperature in the combustion chamber of the internal
combustion engine. The greater the engine load, the higher the temperature in the combustion chamber, and consequently the greater the emission of compounds of atomic nitrogen with oxygen. In addition, the temperature in the combustion chamber largely depends on the composition of the mixture. If the mixture is too depleted or enriched, it releases less heat during combustion, the combustion process slows down and is accompanied by a large loss of heat in the walls, i.e., under such conditions, less NOx.

2. Analysis of factors affecting nitrogen oxide emissions

For diesel engines, the composition of NOx depends on the setting angle of the fuel injection advance and the fuel ignition delay period. With an increase in the setting angle of advance of fuel injection, the ignition delay period extends, the uniformity of the fuel-air mixture improves, more fuel evaporates, and the temperature increases sharply during combustion, so the amount of NOx increases. In addition, with a decrease in the setting angle of advance of fuel injection, the release of compounds of atomic nitrogen with oxygen can be significantly reduced, but the power and economic performance of the diesel engine significantly deteriorates [19-22].

Compounds of atomic nitrogen with oxygen and their derivatives are byproducts of petrochemical production (in the absence of chemically bound nitrogen in the fuel) and the working processes of diesel engines. Obrazujas in the combustion process, mainly as a result of chemical reactions of atmospheric oxygen and nitrogen, they have an impact on the lungs and on the eyes. With prolonged exposure, respiratory function is impaired. Compounds of atomic nitrogen with oxygen irritate the mucous membrane of the eyes and nose, destroy the lungs. In the respiratory tract, compounds of atomic nitrogen with oxygen react with moisture, affect the mucous membranes, bronchi, alveolar tissue of the lungs, etc. Getting into the soil, they wash out the compounds of magnesium, potassium and calcium, as a result, plants do not receive these substances in sufficient quantities for photosynthesis and the leaves turn yellow. Nitrogen dioxide directly affects the leaves, causing partial closure of the stomata, which slows down transpiration and as a result reduces the intensity of photosynthesis.

Once in the atmosphere, compounds of atomic nitrogen with oxygen is gradually converted to dioxide by interacting with ozone and hydroperoxide radicals. Thus, compounds of atomic nitrogen with oxygen accumulate in the lower atmosphere. Their presence causes acid rain, photochemical fog-smog, reduces the transparency of the atmosphere and affects the subsequent transformations of the main component of the atmosphere – oxygen [23, 24].

After analyzing the issue of air pollution by diesel exhaust gases, we can conclude that it is necessary to reduce the content of compounds of atomic nitrogen with oxygen in the exhaust gases. Therefore, the application of poorly studied methods to reduce this toxic component is the main scientific task that requires a practical solution without serious changes in the design of internal combustion engines.

3. Methods for reducing nitrogen oxides in exhaust gases of internal combustion engines

In a diesel engine, fuel is injected into a cylinder already filled with hot compressed air and there is simply no time left for the formation of a full-fledged fuel mixture. Even with the thinnest atomization (for which the pressure is increased), not all fuel microparticles have time to acquire the necessary amount of oxygen molecules - that's soot for you. Lowering the temperature in the cylinder negatively affects the engine power. The main problem of diesel, which has not yet been fully resolved, is the choice between reducing soot and compounds of atomic nitrogen with oxygen emissions: by improving one parameter, we inevitably spoil the second.

Modern comprehensive exhaust gas treatment systems for diesels consist of catalytic and liquid neutralizers, as well as particulate filters [25-28].

In the new generation of soot filters, the General principle remains the same - to detain and destroy soot particles. In the design, the filter is placed immediately behind the exhaust manifold and every 300...500 km of mileage, the controller turns on the multiphase injection mode, increasing the amount of fuel entering the cylinder. In addition, the surface of the filter element is covered with a thin layer of a new catalyst, which further increases the temperature of the exhaust gases to the required 560...600°C.
The filter element consists of a ceramic (silicon carbide) microporous sponge. The thickness of the walls between its channels does not exceed 0.4 mm, so the filter surface is very large. Sometimes this «sponge» is made from an ultra-thin steel fiber, also coated with a new catalyst. The packing is so dense that it holds up to 80% of particles with a size of 20...100 nm.

New filters have become actively involved in the management of the engine. After all, the enrichment mode is activated by a signal from the pressure sensors installed at the inlet and outlet of the filter. When the difference in readings becomes significant, the computer takes it as a sign of clogged «sponge» soot. And the burning is controlled by a temperature sensor [27, 28].

Toyota has developed its own equally effective cleaning system, called DPNR. It simultaneously neutralizes both carcinogenic soot particles and simply harmful compounds of atomic nitrogen with oxygen. The main role is played by a new microporous ceramic filter, covered with a layer of nitrogen-accumulating material and a platinum-based catalyst. When the engine is running on a poor mixture, soot particles are oxidized by atomic oxygen, which is released when NO and O₂ are combined from the exhaust gases during the accumulation of NO₂.

Periodically, when the computer briefly enriches the mixture, these particles are oxidized with oxygen, which now occurs when the accumulated oxides are decomposed into harmless nitrogen.

DPNR showed a reduction in soot and NOₓ content by 80% compared to current standards, but is only applicable for the latest generation of diesels operating with a high-pressure common rail system on a fuel with a reduced sulfur content [27].

One of the alternative methods of neutralization of exhaust gases is the use of low-temperature plasma. Research in Japan, the United States, and Russia has led to the creation of experimental samples of equipment based on plasma technologies.

Low-temperature plasma consists of positively charged ions and negatively charged electrons obtained in special devices with various types of pulsed high-voltage electrical discharges (corona, barrier, etc.), as well as neutral atoms and molecules.

The schematic diagram includes an exhaust gas and oil supply unit, a quartz glass or ceramic tube used as a dielectric barrier, and two electrodes in the form of a stainless steel metal mesh. The discharge device is supplied with a current from a source that generates a voltage pulse with a duration of 250...350 Ms. A barrier discharge occurs at an electrical voltage of 0.5...35 kV and a pulse repetition frequency of 50...2000 Hz.

Diesel exhaust gases are sent to the plasma chemical reactor, having previously been dried in a dehumidifier. In a plasma chemical reactor, these gases are «mixed» with oil. Under the action of an electric discharge in the tubes of the discharge device, soot particles actively absorb oil on their surface. To remove soot, particles of which are located as if in an oil cocoon, an oil separator is used. The soot is collected in a special container, and the oil after additional cleaning in the filter continues to circulate in a closed loop. Thus, it is possible to provide a very high efficiency of absorption of soot particles – up to 100% in the entire range of diesel rpm. From the oil separator, some of the exhaust gases can be sent to the diesel intake manifold (recirculation). This reduces the content of compounds of atomic nitrogen with oxygen in the exhaust [27-29].

The physical and chemical nature of the phenomena occurring under the action of a barrier discharge in a plasma-chemical reactor has not yet been sufficiently studied. However, the process can be simplified in the following way. When a voltage is applied to an electric discharge device, a non-equilibrium weakly ionized low-temperature plasma is created in it, which affects the exhaust gases. As a result of multi-stage chemical reactions, oxides of nitrogen, sulfur and carbon are decomposed into non-toxic molecules of oxygen, nitrogen, sulfur and carbon. At the same time, there is a conversion (conversion) of compounds of atomic nitrogen with oxygen into its dioxide, which is bound by the radical OH to nitric acid in the form of an aerosol. Similar reactions occur with sulfur dioxide and carbon monoxide, leading to the formation of aerosols. Aerosols are captured in fairly simple electrofilters that provide a degree of purification up to 98...99%.

Plasma cleaning is 1.5...2 times cheaper than in existing multi-component devices. No need to use precious metals, significantly increases the resource of neutralization systems, reduces the time for their
maintenance. However, it will be possible to switch to commercial production of plasma chemical reactors (and hence their widespread use) when it is possible to reduce the power consumption for power supply of the reactor. In experimental and experimental systems, they reach 4...5% or more of the diesel power.

Bosch, which is a lambda probe for diesel engines. A lambda probe is a sensor that measures the oxygen content of the vehicle's exhaust gases. Its implementation allows you to optimize the fuel supply to the cylinders, which reduces the toxicity of exhaust gases and reduces fuel consumption, increases the power and torque of the engine, and improves its starting characteristics.

In addition, the lambda probe together with the electronic injection system ensure the operation of the exhaust gas catalytic Converter, which performs its function only when the proportions of the fuel-air mixture are strictly observed.

Today, when the power systems of diesels are controlled by electronics, and their mechanical high-pressure fuel pumps are a thing of the past, the lambda probe has come to the service of these engines. Receiving data on the amount of oxygen in the exhaust, electronic control units of modern diesels adjust the operation of the exhaust gas recirculation system, determine the optimal fuel injection time and boost pressure. Power systems with a lambda probe are particularly effective in full load mode, when the propensity to smoke increases. The physical and chemical nature of the phenomena occurring under the action of a barrier discharge in a plasma-chemical reactor has not yet been sufficiently studied. However, the process can be simplified in the following way. When a voltage is applied to an electric discharge device, a non-equilibrium weakly ionized low-temperature plasma is created in it, which affects the exhaust gases. As a result of multi-stage chemical reactions, oxides of nitrogen, sulfur and carbon are decomposed into non-toxic molecules of oxygen, nitrogen, sulfur and carbon. At the same time, there is a conversion (conversion) of compounds of atomic nitrogen with oxygen into its dioxide, which is bound by the radical OH to nitric acid in the form of an aerosol. Similar reactions occur with sulfur dioxide and carbon monoxide, leading to the formation of aerosols. Aerosols are captured in fairly simple electrofilters that provide a degree of purification up to 98...99%.

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The principle of operation of the SCR system is a chemical reaction of ammonia with nitrogen oxide of exhaust gases, which results in the formation of harmless nitrogen and water vapor.

The well-known total concern has created a safe water-based ammonia substitute that meets DIN 70070 standards. Today, it is widely used in agriculture, the textile industry, as well as in the manufacture of cosmetics and perfumes. This liquid is completely non-toxic.

The selective Converter consists of two main components: directly a catalytic Converter with a cellular structure, mounted in the car's muffler, and an additional tank for the AdBlue ammonia substitute. So installing the SCR system on cars with Euro 5 engines does not require a drastic change in their design [30].

The engine is equipped with an additional module, combined with an electronic motor control system, which accurately doses the amount of AdBlue liquid supplied to the exhaust manifold. It is very important that engines with the SCR system are significantly more economical: for example, long-range trucks consume 30% less fuel. And the higher the savings – the lower the content of harmful substances in the exhaust gases.

Work on SCR cleaning technology was started in the last century. Today, the system is in mass production. Mercedes-Benz trucks and buses were equipped with the SCR system in 2008. Since this year, all Mercedes-Benz cars have had a selective exhaust gas Converter. After a small upgrade of the SCR system, the diesel engines equipped with it will comply with Euro 6 environmental standards.

However, we need to solve another important problem – to create a branched network of special gas stations where AdBlue can be refueled.

4. Evaluating the effectiveness of methods for improving environmental indicators
It should be noted that currently there is no comprehensive assessment of the effectiveness of methods for improving the environmental performance of diesels. It seems appropriate to take into account the cost of the devices themselves and the amount of damage prevented in a comprehensive assessment.

The available methods allow making only relative estimates of the effectiveness of means of reducing emissions, so the further task is to create a system of comprehensive assessment of the proposed methods and means of reducing the toxicity of diesel exhaust gases during their operation. The use of low-toxic work processes can significantly affect the release of compounds of atomic nitrogen with oxygen into the atmosphere. To date, the problem of neutralizing compounds of atomic nitrogen with oxygen in exhaust gases should be solved comprehensively. In order to comply with environmental standards for the chemical composition of exhaust gases, many diesel vehicles will need to have cleaning systems. They make it possible to filter solid particles and reduce NO\textsubscript{X} emissions as effectively as possible. Such systems are called multicomponent, because along with NO\textsubscript{X} and solid particles, they also reduce the content of CH and CO.

The combination of systems requires efficient management of the diesel engine. To date, combinations of the NO\textsubscript{X} storage neutralizer and the particulate filter, as well as the SCR neutralizer and the particulate filter have been developed.

An example of a combined system is the following scheme: soot is continuously oxidized by a filter with a catalytic coating, the SCR system then reduces NO\textsubscript{X} emissions. The additive of the reducing agent is carried out depending on the mode and temperature or on the concentration of NO\textsubscript{X} in the exhaust gases before the neutralizer. The operation of the integrated system is monitored by NO\textsubscript{X} or NH\textsubscript{3} gas sensors and temperature sensors.
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