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Ozone-Catalytic Treatment of Automotive Exhaust

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Abstract

In the paper, an original design of an ozone-catalytic device, in which the process of ozone formation occurs directly inside the catalyst monolith of the honeycomb structure, is proposed for solving the problem of exhaust gases purification at the "cold start" of an automobile engine. For the considered device, various regimes of operation were examined, and the equations allowing us to calculate the concentrations of ozone depending on time were obtained. The developed mathematical model shows a significant decrease in ozone concentration after the "cold start" is over and the temperature of the exhaust gases increases, because of changes in the balance of various chemical reactions. Thus, the ozone concentration is maximum during a cold start, precisely when the lower temperatures do not allow other reactions than those of oxidation of toxic gases with ozone, and decreases by the time the catalytic unit warms up, when effective neutralization of toxic impurities becomes possible without the participation of ozone. The results of the mathematical modeling were confirmed by testing this device for purifying exhaust gases of a YaMZ-238M2 engine. The test results show that the use of ozone-catalytic reactions significantly increases the efficiency of neutralizing toxic impurities under cold start conditions, compared to the case when only catalytic reactions with oxygen without the participation of ozone are used.

1. Introduction

Currently, environmental pollution by exhaust gases from internal combustion engines in large cities (particularly in Moscow) accounts for up to 80% of total emissions, which leads to a constant toughening of standards for the maximum content of toxic impurities in vehicle exhaust gases. One of the ways to solve the problem is to equip domestic engines with imported catalytic converters. However, using a standard “three-way” converter [1–2] does not eliminate the problem of “cold start”, when the catalytic treatment system is not yet heated to the necessary temperature and a significant amount of toxic substances are released into the atmosphere. A similar problem is relevant for the “cold start” of diesel engines [3].

This problem is of a global international nature, and, despite significant efforts made by leading foreign laboratories and companies (Lawrence Livermore National Laboratory, Engelhard, etc.), has not been solved satisfactorily to date.

Various thermal management methods for the solution to this problem were investigated and analyzed in the literature [4]. A simple solution is to locate the catalyst closer to the engine; however, after warming the high exhaust temperature may cause thermal sintering, which shortens catalyst lifetime and compromises its performance. Extra combustion devices, heat storage devices and electrically heated catalysts (EHCs) have been tested to improve light-off performance during warm up. All these approaches require additional expenses of fuel and energy and make the exhaust gas system more complex.

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Also, one of the alternative solutions to the problem of cold start is the use of so-called zeolite "traps" [5], installed in front of the main catalytic converter, which adsorb toxic impurities at the engine warm-up stage and subsequently, when the temperature rises, release these substances for neutralization in the main converter. However, such materials are characterized by extremely low hydrothermal stability and methods based on their use have not become widespread.

A promising method for solving the "cold start" problem is the use of ozone-catalytic technologies, when active molecules of the allotropic modification of oxygen – ozone are used as an oxidizing agent.

The studies performed at the Boreskov Institute of Catalysis showed that introducing ozone into gas streams increases the efficiency of oxidation, allowing an effective catalytic purification at low temperatures, and reducing energy costs and equipment size [6, 7]. Ozone provides effective oxidation of organic compounds, such as toluene, xylene, acetone over copper oxide catalyst at temperatures of 40–60 °C, which is about 200–250 °C lower than the temperatures required for total oxidation of the compounds in traditional catalytic oxidation by air.

This method was found very effective for the removal of difficult-to-oxidize compounds, in particular, chlorine-containing substances and polyaromatic hydrocarbons. For example, in [8] recent advances in the catalytic ozonation of Cl-VOCs at low temperatures were systematically reviewed, including single Cl-VOCs and gas mixtures with Cl-VOCs. The systems examined included chlorobenzene, dichloromethane, dichloroethane, trichloroethane, etc., with a series of catalysts based on oxides of Fe, Mn, Ce, V and Ti. It was shown that the presence of ozone in the gas stream lowered the temperature of the Cl-VOC total oxidation from 300–400 to 80–120 °C.

A version of catalytic ozonation method performed in the liquid phase was described in [9]. A wet scrubbing – catalytic ozonation (WCO) process with the catalyst MnOx on activated coal was developed for the efficient removal of volatile organic compounds from gas streams. Mineralization efficiency, degradation pathway and mechanism, and effects of the process operating parameters were investigated using toluene as the target pollutant. The results showed that the average removal efficiency of toluene reached 71.82% within 90 min under optimal conditions ($C_{Toluene}$ = 100 mg/m^3; C_{Ozone} = 1 mg/L; catalyst loading = 5 g/L; pH = 7; gas flow = 500 mL/min), which outperformed that of a gaseous system.

In [10] a reverse-flow non-thermal plasma (NTP) reactor coupled with catalyst was used for the abatement of toluene. In this study, the toluene degradation performance of different reactors was compared under the same conditions. The mechanism of toluene abatement by NTP coupled with catalyst was explored, combined with the generation of ozone, NO_2, and organic by-products during the reaction process. It was found that a long reverse cycle time of the reactor and a short residence time of toluene decreased the internal reactor temperature, which was not beneficial for the degradation of toluene. Compared with the dielectric barrier discharge (DBD) reactor, toluene degradation efficiency in the double dielectric barrier discharge (DDBD) reactor was improved at the same discharge energy level, but the concentrations of NO_2 and O_3 in the effluent were relatively high; this was improved after the introduction of a catalyst. In the reverse-flow NTP reactor coupled with catalyst, the CO_2 selectivity was the highest, while the selectivity and amount of NO_2 was the lowest and aromatics, acids, and ketones were the main gaseous organic by-products in the effluent.

There are a few works related to the use of non-thermal plasma and ozone in the treatment of automotive exhaust gases. In [11], a significant augmentation of the oxidation rate of carbon monoxide and unburned hydrocarbons has been demonstrated when the two processes of atmospheric pressure dielectric barrier discharge and diesel oxidation catalysis were used simultaneously. With carbon monoxide oxidation, the rate increase was attributed to a heterogeneous reaction of supplied ozone with carbon monoxide. Ozone injection was investigated along with the direct application of the plasma to the gas upstream of a Diesel oxidation catalyst on a Diesel engine test bench. When used on the Diesel engine exhaust in steady-state conditions, depending on the engine regime, the two processes had different effects on the gas composition. Both processes induced heating of the catalyst, but while the plasma treatment of the entire gas flux heated the gas itself (and therefore heating the catalyst), the injection of ozone heated the catalyst solely through the heat of reaction of ozone with adsorbed species. Mechanisms for these effects were proposed and the performance of each approach was discussed in terms of energy cost and technical feasibility. While both techniques gave improvements in emissions, the ozone injection option might be more practical because of lower investment costs. In relation to ozone injection, this study only considered that the ozone generator was fed with pure oxygen, because the efficiency of ozone production using dry air as feed gas would generally be about half the value found in this work.

Non-thermal plasma combined with wood fiber has been investigated for the diesel exhaust purification [12]. The combination of dielectric barrier discharge (DBD) and wood fiber (WF) enhanced the removal efficiency of nitrogen by oxides (NOx) due to the positive activity of oxygen-containing functional groups (such as O–H groups or C–O groups) on the wood surface, which promoted the removal of NOx by 10–13%. In particular, it was observed that, when carbon black was loaded on the wood fiber, there was a simultaneous removal of carbon soot and NOx.

The effect of NTP on the oxidation and removal of different components in particulate matter (PM) in diesel exhausts was studied in [13]. NTP technology can oxidize and decompose diesel by PM under much lower temperatures (≤200 °C) without a catalyst, showing promise for potential applications. A self-made NTP generator was used to produce NTP gas that reacted with PM at a certain reaction temperature and reaction time, and the concentration of O_3 in the NTP was modified by adjusting the working parameters. Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and gas chromatography-mass spectrometry (GC-MS) were used to analyze changes in the surface functional groups, component oxidation activity, removal effect, and the soluble organic fraction (SOF) of PM samples before and after processing. As the O_3 concentration increased, the effect of NTP on PM removal strengthened. PM surface functional groups can be converted from C–OH into C–O under the action of NTP at high O_3 concentrations. The oxidation activity of the volatile fraction (VF) and soot in PM can be substantially improved under high O_3 concentrations. Higher O_3 concentrations resulted in increases in the number of oxygen-containing groups in the molecular formula of SOF and the ratio of components. The performed study provided a certain value for the strategy of removing PM pollutants from diesel.

A study of an NTP device for the treatment of exhaust gases in an internal combustion engine is described in [14]. Several tests using a plasma device to treat exhaust gases were conducted on a Honda GX200-196 cm^3 engine at different rotational speeds. A plasma reactor could be efficient in degrading nitrogen oxides and particulate matter. Monoxide and carbon dioxide abatement were found minimal.

In [15], Chinese scientists showed that catalytic diesel particulate filtration (CDPF) assisted by ozone was a promising strategy for soot elimination at exhaust temperatures. It is important yet challenging to utilize the strongly oxidizing ozone while prevent its escape. In this study, rod-like Mn_2O_3 catalysts with high ozone decomposition ability were proved as an ideal tool for such a task. With thorough characterizations and temperature-programmed oxidation tests in selected atmospheres, triple low-temperature incubation effects were ascribed to the (catalytic) decomposition of ozone, including oxidizing NO to NO_2, breeding surface oxygen complexes on soot and surface manganese species on the catalyst. Superior soot elimination efficiency was achieved by the tandem work of NO_2 (at 200–500 °C), NO_2-induced nitrates/nitrites (at 200–300 °C), surface manganese oxides (at 300–400 °C) and O_2 (at 400–500 °C), indicating the coupling of ozone and transition metal oxides may lead to reliable and cost-effective CDPF systems.

The behavior of the selective catalytic reduction of nitrogen oxides assisted by a dielectric barrier discharge was investigated in [16]. The principal function of the dielectric barrier discharge in the system is to generate ozone, which is continuously fed to a chamber where the ozone and NO-rich exhaust gas are mixed (NO accounts for the large majority of NOx). In the ozonization chamber, a part of NO contained in the exhaust gas is oxidized to NO_2, and then the mixture of NO and NO_2 enters the catalytic reactor. The ozonization method proposed in this study was found to be more energy-efficient for the oxidation of NO to NO_2 than the typical non-thermal plasma process. The degree of NO oxidation was approximately equal to the amount of ozone added to the exhaust gas, implying that the decomposition of ozone into molecular oxygen was relatively slow, compared to its reaction with NO. When the exhaust gas was first treated by ozone to produce a mixture of NO and NO_2, a remarkable enhancement in the catalytic reduction of nitrogen oxides was observed.

Thus, the use of ozone increases the efficiency of catalytic processes, allows for effective catalytic cleaning at low temperatures, and reduces energy costs and equipment size. Ozone provides effective oxidation of difficult-to-oxidize compounds, in particular, chlorine-containing substances and polyaromatic hydrocarbons.

However, if ozone is supplied instead from an external device, during its transportation to the purification zone and directly on the first millimeters of the frontal layer of the catalyst, the “active” ozone molecules recombine into oxygen, which is inert at “cold start” temperatures, which reduces the efficiency of the process. Therefore, the most effective ozone-catalytic processes should be based on the generation of ozone near the catalytic layer or directly in the catalyst layer.

2. Ozone-catalytic exhaust gas purification device

To solve the “cold start” problem the Boreskov Institute of Catalysis SB RAS (Novosibirsk) together with the Department of Electromechanics of the Ufa University of Science and Technology (Ufa) proposed an approach based on the use of devices in which ozone is effectively generated in the entire catalyst bed with minimal energy consumption.

In contrast to the currently used “classical” converters based on catalysts containing noble metals, this device has the following advantages:

- generation of ozone and subsequent neutralization reactions with its participation occur over the entire surface of the catalyst;
- increased efficiency in neutralizing toxic impurities contained in purified exhaust gases;
- it maintains efficiency even at low exhaust gas temperatures, which is especially important during the “cold start” of a car engine;
- smaller weight and dimensions and low energy consumption of the ozone-catalytic device;
- the ozone-catalytic unit can be easily integrated into the existing system for neutralizing exhaust gases of internal combustion engines.

An ozone-catalytic exhaust gas purification device is shown in Fig. 1. A schematic longitudinal section of the device is shown in Fig. 1a. A photograph of the end surface of a block catalyst with a honeycomb structure with embedded electrodes is shown in Fig. 1c.

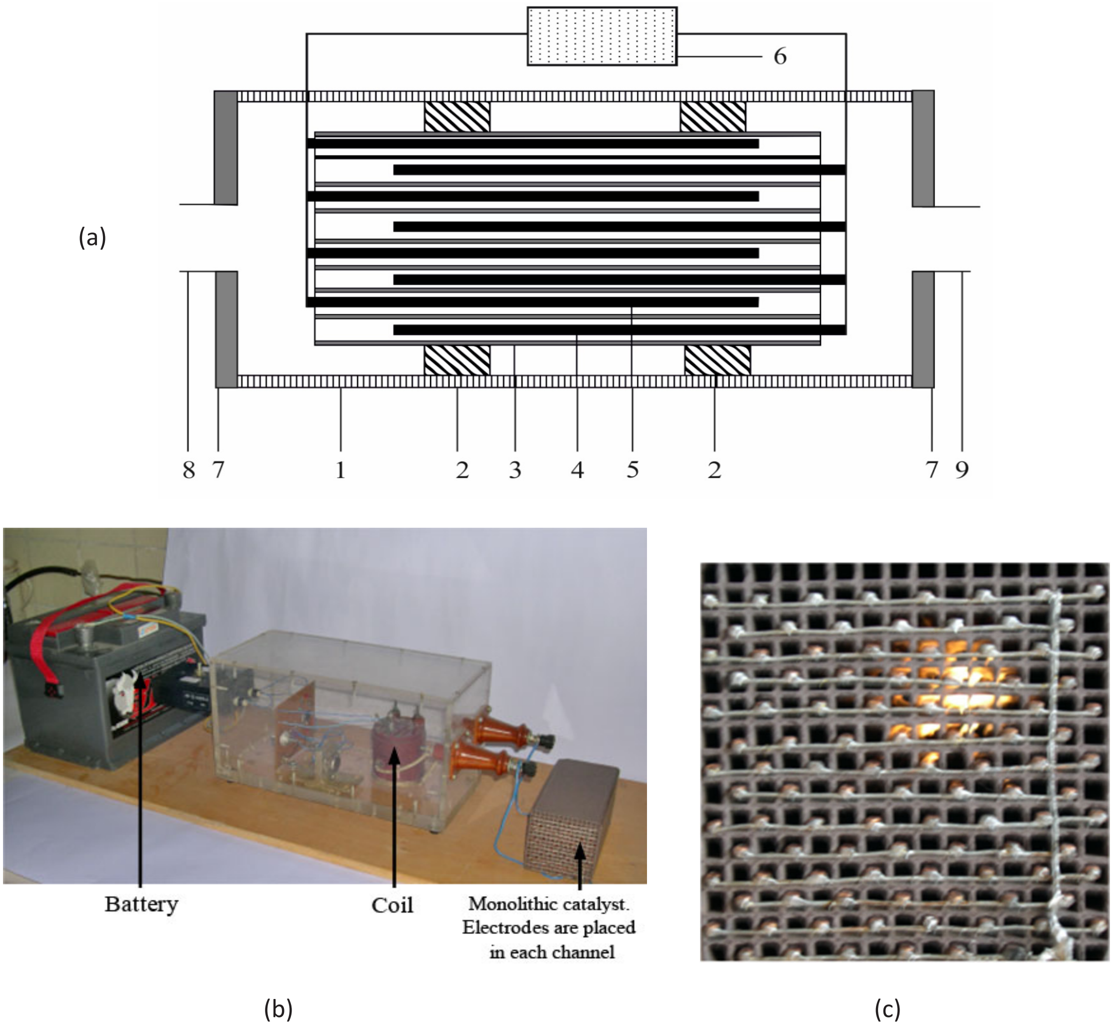

Fig. 1. Ozone-catalytic device for exhaust gas purification: (a) – schematic diagram of the device, longitudinal section; (b) – photograph of a monolithic catalyst, through which channels electrodes are inserted, along with a battery and a demonstration model of a power source; (c) – photograph of a monolithic catalyst, end face view.

The device for cleaning exhaust gases consists of a dielectric housing 1, insulating racks 2, in which a monolithic catalyst of a honeycomb structure 3 is located with its cells containing grounded electrodes, 4, and high voltage electrodes 5, connected to a high-voltage alternating current source 6. At the ends of the dielectric-catalyst monolith of the honeycomb structure there are flanges 7 with an opening 8 for the inlet of the gas mixture with toxic impurities and an opening 9 for the outlet of a gas mixture purified as a result of the ozone-catalytic reactions.

The principle of operation of the device for purifying exhaust gases is as follows. High voltage is supplied to the electrodes 5 from a high-frequency alternating current source 6. As a result of that, a barrier discharge occurs in the channels of the dielectric-catalyst monolith of the honeycomb structure 3. Under the influence of this discharge, the gas mixture passing through these channels is enriched with ozone, which interacts with toxic impurities contained in this gas mixture, and the oxidation reactions of these impurities occur. Thanks to flanges 7, the entire gas flow blown through the housing passes through the channels of the dielectric-catalyst monolith of the honeycomb structure and is purified from toxic impurities, which are oxidized to harmless components. A monolithic catalyst with a honeycomb structure is a dielectric structure consisting of γ-alumina, and iron and chromium oxides as active components.

Due to the porous structure of the channel walls, the dielectric catalytic monolith of the honeycomb structure has a large specific surface area, which increases the efficiency of catalytic reactions. Since the groups of electrodes are located in the channels of the dielectric catalytic monolith in a checkerboard pattern, the number of dielectric barriers increases significantly and, consequently, the generation of ozone and the rate of oxidation of toxic impurities in the passing gas increases.

Experimental studies were conducted to determine the efficiency of ozone formation. As experimental data showed, when pure oxygen was passed through a dielectric catalyst monolith of a honeycomb structure at room temperature, the specific productivity was 72 g of ozone per kWh, which is a high figure [17].

3. Mathematical modeling of ozone formation in exhaust gases

In the case of a barrier discharge occurring in pure oxygen, the formation of ozone mainly occurs as a result of the reaction:

$$O + O_2 + M \rightarrow O_3 + M. \qquad \text{(R1)}$$

At the same time, its decomposition reaction occurs:

$$O + O_3 \rightarrow 2O_2. \qquad \text{(R2)}$$

Atomic oxygen for (R1) is formed in a barrier discharge as a result of the dissociation reaction of oxygen molecules under the influence of electron impact:

$$e^- + O_2 \rightarrow O^+ + O^- + e^- \qquad \text{(R3)}$$

occurring along with the reaction of electron multiplication and ionization of oxygen molecules:

$$e^- + O_2 \rightarrow O_2^+ + 2e^-. \qquad \text{(R4)}$$

Taking into account the reactions (R1) to (R4) and the fact that the concentration of atomic oxygen is proportional to the specific power of the barrier discharge, it can be shown that the ozone concentration changes over time t in accordance with the differential equation:

$$\frac{d[O_3]}{dt} = K_1\left([O_2]_0 - [O_3]\right) - K_2[O_3], \qquad (1)$$

where

$$K_1 = A_1 \exp\left(\frac{-E_{1a}}{RT}\right)\frac{P}{V}; \qquad (2)$$

$$K_2 = A_2 exp\left(\frac{-E_{2a}}{RT}\right)\frac{P}{V}; \qquad (3)$$

P is the active power of the barrier discharge, W; V is the total volume of the channels of the catalytic monolith, m^3; R is the universal gas constant, J/(mol×K); T is the temperature, K; A_1, A_2 are the frequency factors of the reactions (R1) and (R2), respectively; E_{1a} = 2.77 kJ/mol and E_{2a} = 9.66 kJ/mol are the activation energies of reactions (R1) and (R2), respectively; $[O]$, $[O_3]$, $[O_2]$ are, respectively, the concentrations of atomic oxygen, ozone and diatomic molecular oxygen; $[O_2]_0$ is the initial oxygen concentration.

Taking into account the boundary condition $[O_3]$, the solution to Eq. (1) for the time during which the gas mixture passes through the ozonizer has the form:

$$[O_3](t) = \frac{A_1[O_2]_0}{A_1 + A_2\exp\left(\frac{E_{1a}-E_{2a}}{RT(t)}\right)}\left(1-\exp\left(-\frac{P(t)}{V}\left(A_1\exp\left(\frac{-E_{1a}}{RT(t)}\right)+A_2\exp\left(\frac{-E_{2a}}{RT(t)}\right)\right)t\right)\right), \tag{4}$$

where *T(t)* and *P(t)* are functions of the temperature and power of the barrier discharge versus time. Since most of the barrier discharge power is dissipated as heat, in the absence of cooling, the ozonizer begins to heat up over time. A change in temperature, in turn, leads to a change in the power of the barrier discharge.

Frequency factors A_1, A_2 can be determined as a result of experimental studies of ozone formation in a barrier discharge occurring in pure oxygen. For example, when measuring ozone concentration at time t_1 and at $t_2 = 2t_1$ at T = const, the frequency factors can be determined in accordance with the expressions:

$$A_1 = \frac{[O_3](t_2)\cdot\ln(u)\cdot\exp\left(\frac{E_{1a}}{RT}\right)}{[O_2]_0\frac{P}{V}t_1\left(1-\frac{1}{u^{t_2/t_1}}\right)}; \tag{5}$$

$$A_2 = \frac{\frac{\ln(u)}{t_1} - A_1\frac{P}{V}\exp\left(\frac{-E_{1a}}{RT}\right)}{\frac{P}{V}\exp\left(\frac{-E_{2a}}{RT(t)}\right)}, \tag{6}$$

where

$$u = \frac{[O_3](t_2)+\sqrt{\left([O_3](t_2)\right)^2 - 4[O_3](t_1)\left([O_3](t_2)-[O_3](t_1)\right)}}{2\left([O_3](t_2)-[O_3](t_1)\right)}; \tag{7}$$

$[O_3]$ (t_1) and $[O_3]$ (t_2) are experimentally measured values of ozone concentration at times t_1 and t_2, respectively.

In the case of ozone formation in a multi-component gaseous environment, such as exhaust gases, the picture becomes significantly more complicated. Equation (1) in this case should be rewritten as:

$$\frac{d[O_3]}{dt} = A_1\exp\left(\frac{-E_{1a}}{RT}\right)\frac{P}{V}\left([O_2]_0-[O_3]\right) - \left\{A_2\exp\left(\frac{-E_{2a}}{RT}\right)\frac{P}{V}+\sum_{i=3}^{n}A_i\exp\left(\frac{-E_{ia}}{RT}\right)[X_i]\right\}[O_3], \tag{8}$$

where $[X_i]$ is the concentration of the i-th component of the gas mixture (except for ozone and oxygen); E_{ia} is the activation energy of the reaction of ozone interaction with the given i-th component of the gas mixture.

At gas volume flow Q, m^3/s, the solution to Eq. (8) for $t \le V/Q$ has the form:

$$[O_3](t) = \frac{B}{C}\left(1-\exp\left(-\frac{CV}{Q}\right)\right), \tag{9}$$

where

$$B = A_1\exp\left(\frac{-E_{1a}}{RT(t)}\right)\frac{P\left(T(t)\right)}{V}[O_2]_0; \tag{10}$$

$$C = \frac{P\left(T(t)\right)}{V}\left[A_1\exp\left(\frac{-E_{1a}}{RT(t)}\right)+A_2\exp\left(\frac{-E_{2a}}{RT(t)}\right)\right]+\sum_{i=1}^{n-2}A_i\exp\left(\frac{-E_{ia}}{RT(t)}\right)[X_i], \tag{11}$$

where *n* is the number of components in a gas mixture.

Dependences of temperature versus time for exhaust gases have been experimentally measured for several brands of automobiles. This dependence for the “Škoda” brand is shown in Fig. 2.

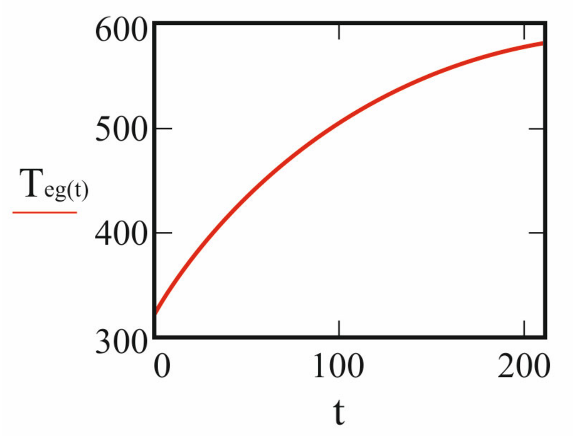

Fig. 2. Dependence of the exhaust gas temperature Teg, K, on the time t, s, elapsed from the moment of the engine start for one of the models of the brand "Škoda".

The temperature dependence of the barrier discharge power P(T(t)) included in (9)–(11) for an ozonizer with a honeycomb structure is determined by the expression:

$$P(T) = 2Nfu_{br}\left(U_{\max} - u_{br}(T)\right)\frac{C_b C_g}{C_b + C_g}\left(1 + \frac{C_b}{C_b + C_g}\right), \tag{12}$$

where C_g is the capacity of the gas gap of the cell, F; C_b is the capacity of the dielectric barrier, F; *f* is the supply voltage frequency, Hz; *N* is the number of cells of a monolithic catalyst into which electrodes are inserted in a checkerboard pattern; U_{max} is the voltage between the electrode and the dielectric barrier of the cell, V; u_{br} is the breakdown voltage, V, depending on temperature:

$$u_{br}(T) = \frac{\pi R_{avg}^2 E_{i,avg} p\delta}{\ln\left(\frac{\pi R_{avg}^2 p\delta}{\ln(1+1/\gamma)kT}\right)kT}, \tag{13}$$

where γ is the coefficient of secondary electron emission; *p* is the gas pressure in the cell; *k* is the Boltzmann constant; δ is the width of the discharge gap; R_{avg}, $E_{i,avg}$ are averaged values of molecular radii and ionization potential for a multi-component gas mixture

$$R_{avg} = \sum_{i=1}^{n} R_i p_i; \tag{14}$$

$$E_{i,avg} = \sum_{i=1}^{n} E_{i,i} p_i, \tag{15}$$

where $E_{i,i}$, R_i, pi are, respectively, the ionization potential, the radius of molecules and the mole fraction for the *i*-th component of the gas mixture.

For further modeling of ozone formation in exhaust gases, the composition of the gas mixture indicated in Table 1 was used.

When ozone is formed in the gas mixture presented in Table 1, a large number of chemical reactions occur with varying intensities. It was assumed, taking into account the known rate constants of chemical reactions [18], that only reactions (R1) – (R4), as well as reactions (R5) and (R6) have a substantial effect on the ozone concentration:

$$O_3 + CO \rightarrow O_2 + CO_2 \tag{R5}$$

$$O_3 + NO_2 \rightarrow O_2 + NO_3 \tag{R6}$$

Table 1. The composition of the gas mixture

Gas mixture component	N_2	O_2	H_2O	CO	CO_2	NO_2
Molar fraction, %	74	8	5	0.1	12.5	0.4
Ionization potential E_i, eV	14.53	13.61	12.62	14.01	13.73	10
Molecule diameter, d, nm	0.364	0.346	0.265	0.359	0.33	0.382

The parameters of reactions (R5) and (R6) are given in Table 2.

Table 2. The parameters of chemical reactions (R5) and (R6) [18]

Chemical reaction	Activation energy E_a, J/mol	Frequency factor A, m^3/s
$O_3 + CO \rightarrow O_2 + CO_2$	13550	10^{-20}
$O_3 + NO_2 \rightarrow O_2 + NO_3$	20360	1.2×10^{-19}

In this case, taking into account reactions (R1) – (R6), the change in ozone concentration is determined by the expression:

$$\frac{d[O_3]}{dt} = K_1\left([O_2]_0 - [O_3]\right) - \left\{K_2 + K_3[NO_2] + K_4[CO]\right\}[O_3], \tag{16}$$

where $[NO_2]$, [CO] are concentration of nitrogen oxide and carbon monoxide, respectively; K_3, K_4 are respectively, the rate constants of chemical reactions (R5) and (R6):

$$K_3 = A_3 \exp\left(\frac{-E_{3a}}{RT}\right); \tag{17}$$

$$K_4 = A_4 \exp\left(\frac{-E_{4a}}{RT}\right). \tag{18}$$

The solution to Eq. (16) has the form:

$$[O_3](t) = \frac{K_1[O_2]_0}{\left\{\begin{matrix} K_1 + K_2 + K_3[NO_2] + \\ K_4[CO] \end{matrix}\right\}}\left(1 - \exp\left(-\left\{\begin{matrix} K_1 + K_2 + K_3[NO_2] + \\ K_4[CO] \end{matrix}\right\}\frac{V}{Q}\right)\right) \tag{19}$$

Taking into account the above-mentioned experimentally measured dependence of the temperature of the exhaust gases on time (Fig. 2), as well as considering the dependences of the power of the barrier discharge and of the rates of chemical reactions on temperature (Eqs. (1), (2), (12) to (15) and (17) to (19)) and taking into account the reaction frequency factors of (R1) and (R2), calculated on the basis of experimental data [17], according to (5) – (7), we can obtain the time dependence shown in Figure 3 for ozone concentration in the specified exhaust gases when they exit the ozonizer with honeycomb structure (at Q = 2 m^3/h).

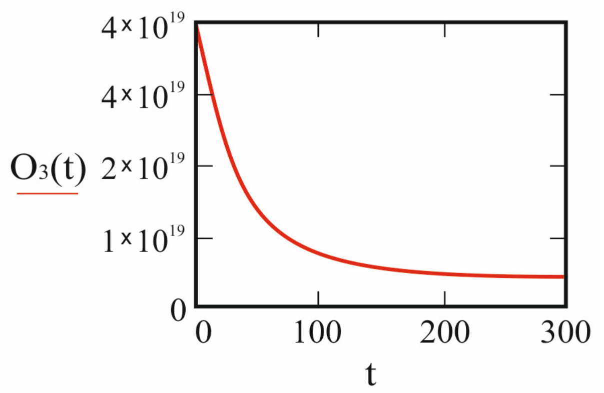

Fig. 3. Dependence of the ozone O_3 concentration, molecules per m^3, on the time t, s, elapsed from the moment of the “Škoda” engine start.

During the passage of the gas mixture through the channels of the catalytic unit, the ozone concentration drops significantly due to simulated reactions with NO_2 and CO, which leads to the conversion of these oxides. As can be seen from Fig. 3, as the temperature of the exhaust gases increases, the ozone concentration decreases significantly, but by this time, the catalytic purification reactions become effective without the participation of ozone due to the heating of the catalyst.

The dependence of ozone concentration on exhaust gas temperature is shown in Fig. 4.

The drop in ozone concentration as the temperature of the exhaust gases increases occurs, among other things, due to a certain decrease in the power of the barrier discharge (see Fig. 5).

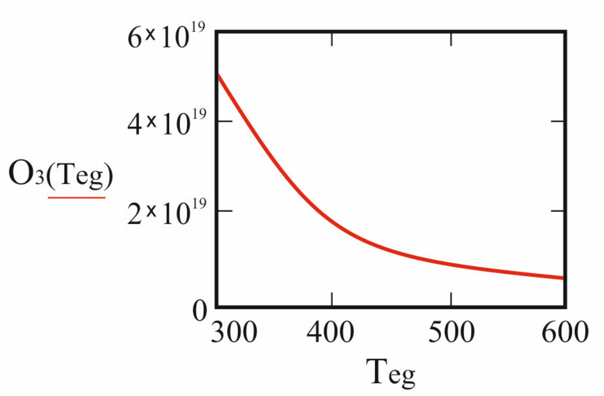

Fig. 4. Dependence of the ozone (O_3) concentration, molecules per m^3, on the exhaust gas temperature T_{eg}, K.

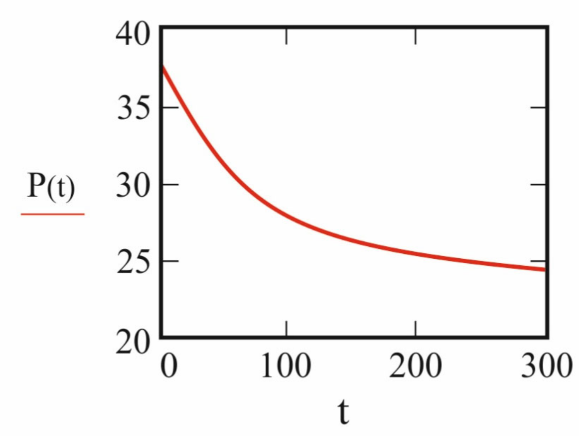

Fig. 5. Dependence of the barrier discharge power P, W, on the time t, s, elapsed from the moment of the "Škoda" engine start.

4. Experimental studies of ozone-catalytic exhaust gas purification

Testing of the ozone-catalytic device was carried out in Dmitrov at the Scientific and Research Center for Automotive Vehicle Testing and Refinement FSUE "NAMI" (NICIAMT FSUE "NAMI") using a test bench with instruments and devices corresponding to GOST R41.49-2003 (UNECE regulations # 49) and GOST R41.24-2003 (UNECE regulations #24). The schematic diagram of the test bench is shown in Fig. 6.

The test bench included: 1 – YaMZ-238M2 engine No. 8845115; 2 – inductor brake B-300, ZOLLNER; 3 – fuel flow meter 730, AVL; 4 – air flow meter 50MRZ-6, MERIAM; 5 – complex gas analyzer ERA125; 6 – smoke meter CEB200, AVL; 7 – differential pressure sensor; 8 – device for determining the temperature of exhaust gases; 9 – neutralizer containing an ozone-catalytic device.

The control unit of the ozone-catalytic device was powered by a 14 V voltage source (ST 190 battery) and included a rectangular pulse generator with an adjustable frequency of 50–250 Hz; an electronic switch; and a high-voltage transformer type 27.3705 (17–25 kV on the high voltage side).

During the tests, the ozone-catalytic device was combined with reactors with a bulk granular catalyst, and the two arrangements of the ozone-catalytic unit were investigated: before and after the location of the reactors with the bulk granular catalyst along the flow of the purified gas (Fig. 7).

The tests were carried out using L-0.2-62 fuel (according to GOST 305-82). The test results for both schemes, performed at a power supply frequency of the ozone-catalytic device of 250 Hz, are presented in Figs. 8 and 9. Temperature dependences of the efficiency of cleaning the exhaust gases of the YaMZ-238M2 engine from nitrogen oxides, carbon monoxide and hydrocarbons under "cold" start conditions for scheme I is shown, in Fig. 8a – 8c, and for scheme II respectively, in Fig. 8d – 8f.

The dependences of the efficiency of exhaust gas cleaning under cold start conditions on the engine load for scheme II with the ozonizer on and off is shown in Fig. 9.

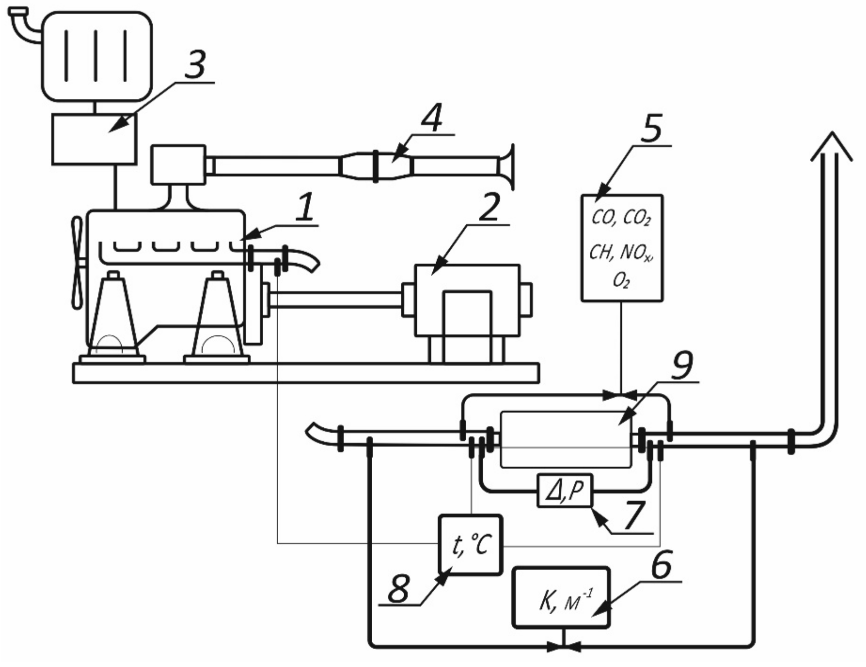

Fig. 6. The schematic diagram of the test bench.

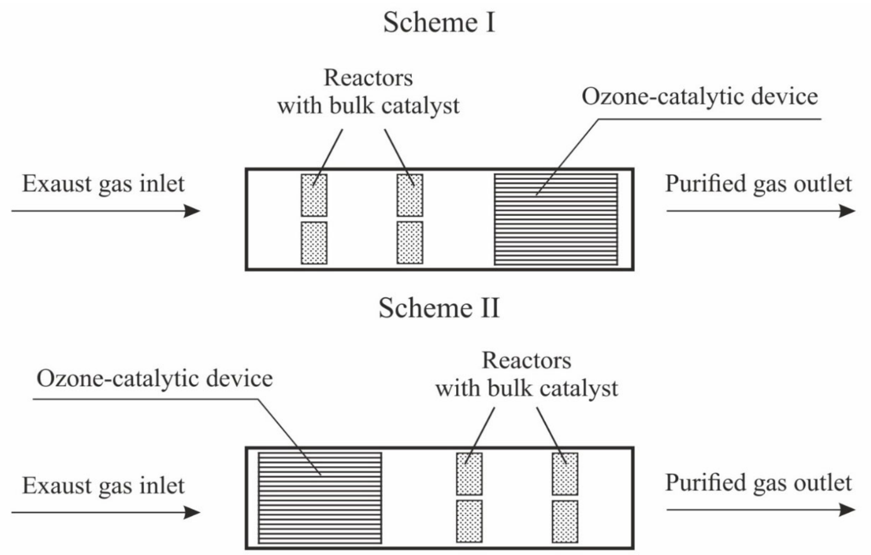

Fig. 7. Schemes of the arrangement of ozone-catalytic unit with the bulk granular catalyst reactors.

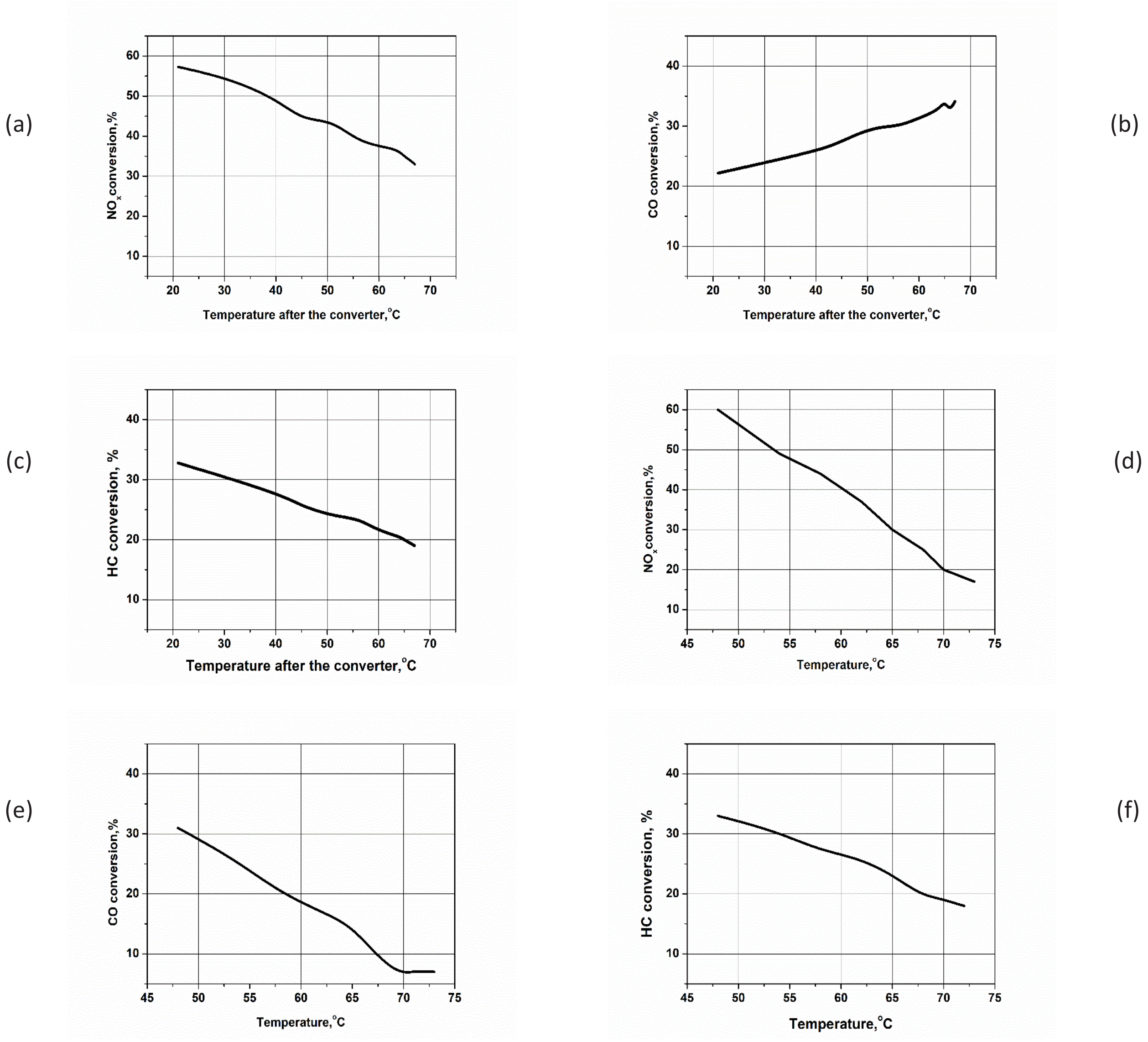

Fig. 8. Results of tests on the efficiency of cleaning exhaust gases from various toxic components versus temperature: 8a – 8c for the arrangement of the ozone-catalytic unit according to scheme I (see Fig. 7); 8d – 8f for the ozone-catalytic unit assembled as in scheme II.

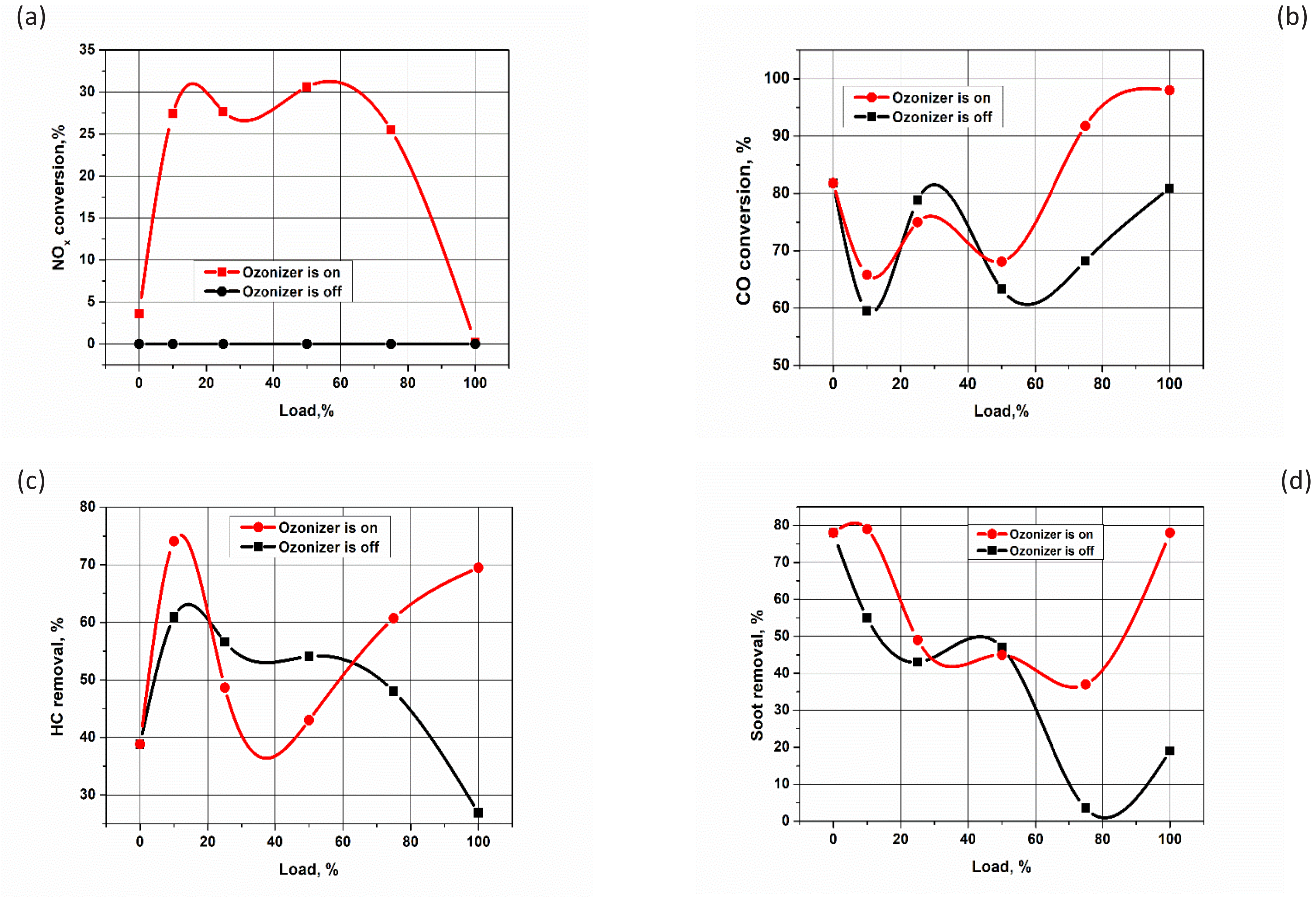

Fig. 9. Results of testing the efficiency of exhaust gas purification versus the engine load: (a) – conversion of nitrogen oxides; (b) – conversion of carbon monoxide; (c) – degree of the removal of hydrocarbons; (d) – soot removal efficiency.

Summarized test results are shown in Table 3. As can be seen from the results presented, the use of an ozone-catalytic device according to scheme I, when it is located at the end (along the gas flow) of the neutralizer, provides more effective purification of exhaust gases from toxic components.

This result may be explained by the presence of conductive soot particles in the exhaust gases, the deposition of which (especially at low temperatures) on the front surface of the catalytic monolith leads to a shorting in electrical circuits, thereby, reducing the efficiency of barrier discharge and ozone generation. When using an ozone-catalytic device according to scheme I, soot is partially captured in the reactors with the bulk granular catalyst, and the negative impact of soot particles is less pronounced.

During testing in accordance with UNECE Regulation No. 49-02 (with increasing engine load) both layouts of the ozone-catalytic device show comparable results in the conversion of the main toxic components, which suggests that by increasing the load and temperature in the converter, the soot is burned and its negative impact is reduced and leveled out when using either scheme.

Table 3. The amounts of the removed components from exhaust gases in the “cold start” mode when using various layouts of the ozone-catalytic unit in the converter

Scheme	The amount of the removed component (mg/m^3)		
	NOx	CO	CH
Scheme I	260.8	522	456.8
Scheme II	184.2	225.5	366

Table 4 provides comparative data demonstrating the increased efficiency of exhaust gas neutralization when using an ozone catalytic device. The results are given as the average of the conversions with a loading range between 60% and 100%. These loads are typical when operating vehicles with diesel engines.

As can be seen from the data presented, the use of an ozone-catalytic device leads to a significant increase in the efficiency of the neutralization of exhaust gases.

Table 4. Comparative data on the conversion of waste gas components

Experiment	Conversion, %			
	NOx	CO	CH	Soot
Ozonizer is off	0	65	30	30
Ozonizer is on	25	>95	70	65

Figure 10 shows a comparison of the experimentally measured dependence of carbon monoxide conversion on exhaust gas temperature (shown in Fig. 8b) and the same dependence obtained as a result of calculations based on the mathematical model given in section 3 (i.e., taking into account the temperature dependences both for the concentration of ozone in the gas mixture under consideration and for the rate constant of the reaction of its interaction with carbon monoxide).As can be seen, there is a good correspondence between the theoretical and experimental results.

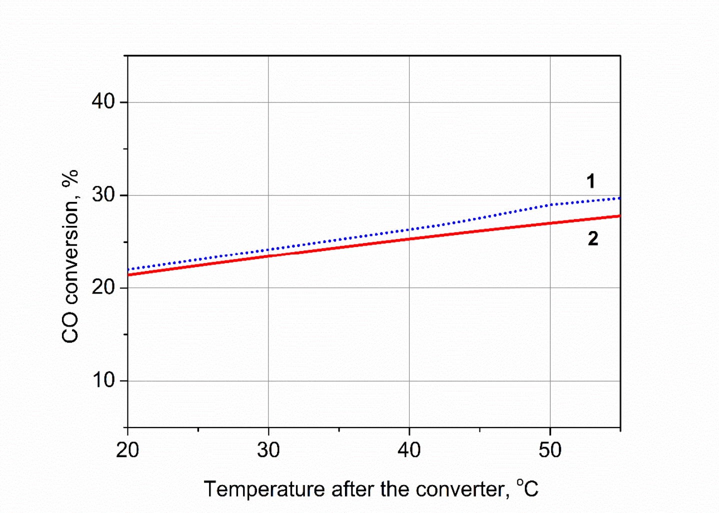

Fig. 10. Comparison of experimental (1) and calculated (2) dependences of carbon monoxide conversion on temperature for a gas mixture passing through an ozone-catalytic device.

5. Comparison of the results obtained with the world level of research in this area

A targeted work on the study and development of ozone-catalytic devices for purification of exhaust gases from diesel engines was carried out at the University of Karlsruhe (Germany) [19].

In this study, with the main goal to create an effective ozone catalytic device for neutralizing nitrogen oxides using the Plasma-Assisted Catalytic Reduction concept, the patterns of ozone generation in a barrier discharge were studied, testing the developed device on laboratory scale and on a pilot stand for the neutralization of exhaust gases of the diesel engine.

A brief comparative description of the ozone-catalytic device considered in this article and the device described in [19] is given in Table 5.

There it is shown that the characteristics of our ozone-catalytic converter are superior in its functionality to the prototype described in [19].

6. Conclusions

A device has been developed for the ozone-catalytic purification of exhaust gases. This device has the advantage that ozone formation occurs directly inside the catalytic unit, which has a honeycomb structure, which ensures high efficiency in neutralizing toxic impurities even at low temperatures (about 50 °C). This allows solving the problem of “cold start” of internal combustion engines and is of great importance from an environmental point of view.

The advantages of this device are also small weight and dimensions and low energy consumption.

A mathematical model of ozone formation in this ozone-catalytic device during the passage of exhaust gases through a barrier discharge plasma in the channels of a honeycomb catalytic monolith,

Table 5. Comparative characteristics of the ozone-catalytic device presented in this paper and the device described in [19]

Comparative characteristics	The device described in [19]	The ozone-catalytic device of this work
Ozone generation	Ozone generation is conducted in an external device (Fig. 5.2 in [19]). Ozone losses	Ozone generation is conducted directly in the catalyst
Catalysts used	Catalysts bases on noble or precious metals, the content of Pt, Ag is 2 wt.%	Metal oxide catalysts
Gas hourly space velocity, h^{-1}	16000 ÷ 60000	> 100000
The range of operation temperatures, °C	100 ÷ 450	20 ÷ 450
Achieved NOx conversion at "cold start" conditions	Not studied	30 ÷ 60

which contains electrodes connected to a high-voltage power source, has been developed. This model shows that most of the generated ozone will be utilized directly in the channels of the catalytic monolith due to reactions with toxic impurities contained in the exhaust gases, primarily nitrogen oxides and carbon monoxide.

The developed mathematical model also shows a significant decrease in ozone concentration as the temperature of the exhaust gases increases in the first minutes of engine operation because of changes in the balance of various chemical reactions, as well because of a slight decrease in the power of the barrier discharge. Thus, the ozone concentration is maximum during a cold start, when catalytic reactions without its participation would not be effective enough, and decreases by the time the catalytic unit warms up, and effective neutralization of toxic impurities becomes possible without the participation of ozone.

In addition, experimental studies of ozone formation in this ozone-catalytic device and the use of this device for purifying exhaust gases of the YaMZ-238M2 engine No. 8845115 were carried out at the Dmitrov test site of the Federal State Unitary Enterprise NICIAMT. The test results show that the use of ozone-catalytic reactions significantly increases the efficiency of neutralizing toxic impurities under cold start conditions compared to the case when only catalytic reactions with oxygen without the participation of ozone are used.

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