Investigation of ozone concentration in the ozone-catalytic device for exhaust gas purification

F R Ismagilov, I Kh Khairulin, D V Maksudov and M V Okhotnikov

Department of Electromechanics, Federal State Budgetary Educational Institution of Higher Education «Ufa State Aviation Technical University» (USATU), K. Marx 12, Ufa, The Republic of Bashkortostan, 450008, Russian Federation

E-mail: md77@list.ru

Abstract. In the paper an original design of the ozone-catalytic device, in which the process of ozone formation occurs directly inside the catalytic block of the honeycomb structure, is proposed for solving of problem of exhaust gases purification at a cold start of an automobile engine. For considered device the regime of operation at the absence of cooling is considered and the equations, allowing us to calculate the degree of heating and the decrease of the stationary concentration of ozone depending on the time, are obtained. Results of mathematician modelling were confirmed by experimental researches.

1. Introduction

In the modern world, more and more attention is paid to ecology. One of the most powerful factors of environmental pollution is automobile transport. In this regard, the questions of neutralization of toxic impurities contained in the exhaust gases have significant meaning.

In modern cars for this purpose, various catalysts are used, for example, platinum catalysts. However, it does not solve the problem completely, since the catalyst does not cope with its function in the first minutes of engine operation. It is the cold start time (the first minutes after starting the engine at a temperature below +5°C) is the most dangerous from the point of view of ecology since, during this period:

- exhaust gases have a low temperature (50-70°C) and contain the greatest amount of toxic impurities due to incomplete combustion, which is manifested by the presence of black smoke at the exit;
- the neutralizer is still not warmed up and its efficiency is extremely low.

The climate of central Russia causes cold start conditions on average 250 days in a year. The amount of emissions from a single cold start is equivalent to 100 km of run, i.e. it is up to 100–200 g. In winter, after starting a cold engine, 90% of all harmful emissions of CO and CH occur exactly during the first kilometers of a car moving.

Figures 1 and 2 for some car brands show the results of experimental studies of the dependence of exhaust gas temperature on time and the concentration of toxic impurities contained in them during the first minutes of engine operation.
2. Formulation of the problem
For solvation of the cold start problem researchers of the Electromechanics Department of the Ufa State Aviation Technical University, together with the Catalysis Institute of the Siberian Branch of the Academy of Sciences (Novosibirsk), have developed an ozone-catalytic device that allows the generation of ozone directly inside a catalyst block of a honeycomb structure [1;2]. The design of this device is shown in figure 3. The introduction of ozone into gas streams increases the efficiency of oxidization of toxic impurities of exhaust gases, allows working at low temperatures, and reduces operating costs and equipment size. Ozone provides effective oxidation of difficult-to-oxidize compounds such as chlorine-containing substances and polyaromatic hydrocarbons.

Figure 1. The dependence of the temperature of exhaust gases on the engine operation time.

Figure 2. Dependence of emission concentration on engine operation time.

Figure 3. Ozone-catalytic device.
Experimental studies have shown that ozone-catalytic reactions produce a high degree of purification even at low temperatures and already at 50°C the average cleaning efficiency of exhaust gas from harmful impurities (carbon monoxide, carbon black, NO\textsubscript{x}) is 94% [3].

Thus, this ozone-catalytic device allows to solve the problem of “cold start”, effectively neutralizing emissions at low temperatures, as well as cleaning the catalyst itself, prolonging its service life.

However, ozone generation is necessary only in the first minutes of engine operation, since, on the one hand, the exhaust gas temperature becomes sufficient for effective catalytic reactions without ozone, and on the other hand, it should be noted, the excessive ozone, which has not yet decomposed, effects harmful influence, for example, on the car’s tires and on the road surface. That is why automatic power supply control based on an electronic control unit associated with a temperature sensor was implemented.

In connection with the above an interesting problem is the study of the dependence of the concentration of ozone in the ozone-catalytic device on temperature and time during the first minutes of the engine operation, when the sensor have not yet sent the signal for switching off and the ozone generation continues.

3. Dependence of the concentration of ozone on temperature

The main reaction of ozone generation inside the described above ozone-catalytic device [4;5]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

(R1)

where atomic oxygen is formed during the barrier discharge process. At the beginning of the ozonizer operation, the ozone concentration increases, until a significant contribution of antagonistic decomposition reactions appears. The main ozone decomposition reaction [4;6]

\[
\text{O} + \text{O}_3 \rightarrow 2\text{O}_2
\]

(R2)

Activation energy for ozone formation reaction \( E_1^f = 0.66 \text{ kcal/mol} \), for decomposition reaction the activation energy is sufficiently higher \( E_2^f = 2.3 \text{ kcal/mol} \).

The kinetic equation of the reversible ozone formation reaction is written in the following form [4;7;8]

\[
\frac{d[O_3]}{dt} = K_1[O_2]^{\gamma_1} - K_2[O_3]^{\gamma_2}
\]

(1)

where \([O_3]\) is the concentration of ozone, mol/L; \([O_2]\) is the oxygen concentration, mol/L; \(K_1, K_2\) are the constants of the reactions of the formation R1 and the decomposition R2 of ozone; \(\gamma_1,\gamma_2\) are the orders of reactions of the formation of R1 and the decomposition R2 of ozone.

At \(\gamma_1=\gamma_2=1\) we determine the equilibrium-stationary value of the ozone concentration, by equating to zero the right side of equation (1)

\[
K_1[O_2] - K_2[O_3] = 0
\]

(2)

hence the concentration of ozone relative to oxygen

\[
\frac{[O_3]}{[O_2]} = \frac{K_1}{K_2}
\]

(3)

In accordance with the Arrhenius equation of the speed of reactions R1 and R2 respectively

\[
K_1 = A_1 \exp\left(-\frac{E_1^f}{RT}\right)
\]

(4)

\[
K_2 = A_2 \exp\left(-\frac{E_2^f}{RT}\right)
\]

(5)
where $R$ is the universal gas constant, $R=8.31 \text{ J/(mol*K)}$; $E_a^1$, $E_a^2$ are the activation energy of reactions R1 and R2; $A_1$, $A_2$ are constants of reactions R1 and R2; $T$ is the temperature, °K.

Taking into account equations (3)-(5), the ratio of ozone concentrations at different temperatures

$$\frac{[O_1](T_1)}{[O_1](T_2)} = \frac{K_1(T_1)/K_2(T_1)}{K_1(T_2)/K_2(T_2)} = \frac{K_1(T_1) \times K_2(T_2)}{K_1(T_2) \times K_2(T_1)}$$

(6)

where $[O_3](T_i)$, $K_1(T_i)$, $K_2(T_i)$ are values of ozone concentration, and also of coefficients $K_1$ and $K_2$ at different values of temperature $T_i$.

Taking into account (4)-(6) concentration ratio is

$$\frac{[O_1](T_1)}{[O_3](T_2)} = \frac{\exp(-E_a^1 / RT_1) \exp(-E_a^2 / RT_2)}{\exp(-E_a^2 / RT_2) \exp(-E_a^1 / RT_1)} = \exp \left( \frac{\Delta T (E_a^2 - E_a^1)}{RT_1} \right)$$

(7)

where $\Delta T = T_2 - T_1$.

Since $E_a^2 > E_a^1$ as the temperature increases, the ozone concentration will decrease.

4. Heating of the ozonizer at the absence of cooling

The active power of the barrier discharge $P$ of the ozone-catalytic device developed at the Department of Electromechanics, the design of which is shown in figures 4-5, is calculated by the formula [4]

$$P = 4NV_s f \left( (V - V_s) c_d - V_s c_g \right)$$

(8)

where $V_s$ is the burning voltage; $V$ is the amplitude value of the voltage; $c_d$ is the dielectric capacity of the cell barrier; $c_g$ is the gas capacity in the discharge gap; $N$ is the number of cells of the catalytic block; $f$ is the frequency.

Most of this power is converted into thermal energy and, taking into account the design of the ozone-catalytic device, it can be said that heat-release occurs evenly throughout the volume of the catalytic block.

Figure 4. Ozonizer of honeycomb structure, view in frontal section.

The capacitance of dielectric barriers $c_d$, by which are the honeycomb cells walls, is defined as

$$c_d = \frac{\varepsilon \varepsilon_0 Lh}{d}$$

(9)
where \( \varepsilon \) is the relative permittivity of the catalytic material, \( \varepsilon = 9.34 \) [2]; \( \varepsilon_0 \) is the electric constant, \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m} \); \( L \) is the length of the catalytic block; \( h \) is the width of the honeycomb cell; \( d \) is the thickness of the cell wall.

Taking into account the relatively low volumetric velocity of the gas-air mixture moving through the catalytic unit, as well as high thermal conductivity and low heat capacity of the catalytic material, we solve the problem of catalytic block heating simplistically, assuming that all heat transfer occurs exclusively through the side walls of the total area \( S = 3LH \), where \( L \) is the length of the catalytic block, \( H \) is its height and width.

Then the temperature change rate of the catalytic block is

\[
\frac{dT}{dt} = \frac{P - T \alpha S}{mC}
\]  

(10)

where \( T \) is the temperature of the catalytic block relative to the environing air temperature (the temperature distribution inside the catalytic block is assumed to be uniform in its volume); \( t \) is time; \( \alpha \) is the coefficient of heat transfer between the surface of the catalytic block and the environing air; \( m \) is the mass of the catalytic block; \( C \) is the heat capacity of the catalyst.

The solution of this equation is

\[
T(t) = \text{Const} \times \exp\left(\frac{-\alpha St}{mC}\right) + \frac{P}{\alpha S}
\]  

(11)

where \( \text{Const} \) is the constant which is determined from the boundary condition corresponding to the temperature of the catalytic block at the initial moment of time (which is taken as zero)

\[
T(0) = 0
\]  

(12)

Then the final solution of the equation is

\[
T(t) = \left(\frac{P}{\alpha S}\right) \times \left(1 - \exp\left(-\frac{\alpha St}{mC}\right)\right)
\]  

(13)

5. Experimental researches

Heating of the catalytic block in the absence of cooling during ozone generation leads to a decrease of the stationary concentration of ozone in accordance with (7). Substituting (13) into (7) allows us to find the dependence of the stationary concentration of ozone (relative to the initial value of the
corresponding parameter) on the time of ozone generation. The results of calculations using the design parameters of the ozone-catalytic device under consideration are shown in figure 6.

The calculated curve can be compared with the results of experimental researches, conducted with given ozone-catalytic device. During these researches ozone was generated from air in the absence of cooling. The curve in figure 7 shows the experimentally detected decrease of the ozone concentration after reaching of the maximum value, taken as a unit.

Conclusion
An original design of the ozone-catalytic device, in which the process of ozone formation occurs directly inside the catalytic block of the honeycomb structure, is proposed [2]. Given design allows us to solve the problem of the cold start of an automobile engine, providing a high efficiency of cleaning of exhaust gases even at a low temperature, when catalytic reactions are not sufficiently effective. Thermal and physicochemical processes in the ozone-catalytic device of the proposed design are considered.

As a result of the analysis of the kinematic equation of the reactions of formation and decomposition of ozone, taking into account the known ratio of activation energies for these reactions, it has been shown that with increasing of temperature there is a decrease of stationary ozone concentration.

The regime of operation of the ozone-catalytic device at the absence of cooling is considered. The equations, allowing us to calculate the degree of heating of the considered device and the decrease of the stationary concentration of ozone depending on the time elapsed from the moment of the start of ozone generation, are obtained.

Experimental studies have confirmed the theoretically predicted trend of an exponential decrease of the concentration of ozone in the first minutes of the ozone-catalytic device at the absence of cooling.
Thus, the operation of the ozone-catalytic device in the regime of switched on generation of ozone is characterized by a gradual decrease of the ozone yield as the exhaust gases warming up and the efficiency of the catalytic reactions increase, which allows not only to solve the problem of a cold start of an automobile engine, but also to avoid excessive ozone influence on tires and the road surface.

References

[1] Ismagilov F R and Maksudov D V 2016 Electric and magnetic fields and gas-discharge processes in heterogeneous dielectric environments (Moscow: Mashinostroenie)

[2] Ismagilov F R, Ismagilov Z R, Khairullin I Kh, Fattakhov R K and Maksudov D V 2003 Ozonizer, Patent RU2196730C1, IPC C01B13/11, Bul. 18

[3] Maksudov D V, Ismagilov F R, Khairullin I Kh, Khairulin S R and Ismagilov Z R 2002 Study of Ozone Generation in the Bed of Heterogeneous Catalysts of Various Geometry Eurasian ChemTech J. 4 pp 271-5

[4] Samoilovich V G, Gibalov V I and Kozlov K V 1989 Physical chemistry of the barrier discharge (Moscow: Moscow State University Press)

[5] Marinov D, Guerra V, Guaitella O, Booth J-P and Rousseau A 2013 Ozone kinetics in low-pressure discharges: vibrationally excited ozone and molecule formation on surfaces Plasma Sources Science and Technology 22(5)

[6] Wei L S, Peng B F, Li M and Zhang Y F 2016 A numerical study of species and electric field distributions in pulsed DBD in oxygen for ozone generation Vacuum 125 123-32

[7] Takic L et al 2004 A study on the kinetic of ozone decomposition in water of different quality Hemijska Industrija 6

[8] Kamalu C I O et al 2015 Modeling the kinetics of ozone layer depletion using systems of ODEs Int. J. of Renewable Energy Technology Research 4(5) 1-11