

The process of oxidation of molecular nitrogen by high-energy oxidants, such as nitric acid vapor, products of the thermolysis of nitric acid, and hydrogen peroxide, in a cold plasma stream was studied. To implement the process of obtaining nitric acid from atmospheric air using reproductive technology (Zakharov's method), the design of a reactor for obtaining nitrogen oxides by direct oxidation of nitrogen in a cold plasma stream is proposed. At the same time, it was proposed to use the effect of obtaining nitrogen oxides in an air mixture with nitric acid vapors (the Karavaev effect) and during the thermal decomposition of hydrogen peroxide with atmospheric nitrogen (the Nagiev effect). The effectiveness of the use of cold plasma for the oxidation of atmospheric nitrogen was established, which is confirmed by the obtained dependences. It is shown that the amount of nitrogen oxides that are formed depends on the efficiency of the formation of a stable flow of OH- radicals in the plasma flow. It was also found that the amount of nitrogen oxides depends on the parameters of the plasma generator, the composition of the liquid used in the burner, and the amount of air supplied.

The effect of nitric acid, hydrogen peroxide, and alcohols as activators of atmospheric nitrogen oxidation in a high-energy field was revealed. It was determined that when comparing three activator substances, which are able to form OH- radicals during their decomposition, it is hydrogen peroxide that is the most promising activator substance for carrying out the process of atmospheric nitrogen oxidation in the plasma flow.

The amount of nitrogen oxides formed in the cold plasma region is almost independent of the flow rate of the reaction mixture through the reactor and remains almost unchanged in a wide range of changes in flow rates from 30 to 3000 l/h

**Keywords:** molecular nitrogen, direct oxidation, cold plasma, nitrogen oxides, nitric acid, plasma torch, activator substance, hydrogen peroxide

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# DETERMINING THE POSSIBILITY OF USING COLD PLASMA FOR THE OXIDATION OF ATMOSPHERIC NITROGEN INTO NITROGEN OXIDES AND THE INFLUENCE OF ACTIVATING SUBSTANCES ON THE PROCESS

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## 1. Introduction

Nitrogen, or Nitrogen, is one of the key chemical elements necessary for sustaining life on planet Earth. The role of nitrogen in nature and human life is extremely important. This element is part of all living organisms and plays an essential role in many biochemical processes. Its presence in proteins, which are key nutrients for animals and humans, is especially important. Nitrogen has a significant impact on the vital activity of plants and animals. In its natural state, it is mainly present in the form of low-activity N<sub>2</sub> molecules in atmospheric air. However, nitrogen is a stable substance, and in the synthesis of proteins in plant and animal organisms, not molecular nitrogen is used but its chemical compounds.

The problem of nitrogen fixation is the transformation of atmospheric nitrogen into compounds with nitrogen, which can be assimilated by plants directly or through previous, relatively simple chemical transformations. This is defined as a vital problem for humanity since the successful solution of this task makes it possible to solve the problem of global nutrition to a large extent, especially in connection with the constant growth of the world population.

In addition, nitrogen compounds are widely used in industry for the production of intermediate products, dyes, plastics, chemical fibers, medicines, and other materials. They are also of great importance in the production of explosives and incendiaries.

For industrial use, deposits of nitrogen-containing compounds (for example, sodium nitrate) are available. The

largest deposits of sodium nitrate are located on the coast of Chile and in South Africa. But this does not solve the problem of providing the growing needs for these compounds.

Therefore, a technical method for binding atmospheric nitrogen is of great importance for the development of the entire chemical industry, strengthening the defense of the state, and meeting the household needs of people.

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## 2. Literature review and problem statement

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It is the molecular nitrogen of the air that is of greatest interest as a raw material. This resource is almost unlimited, available anywhere on the planet, and has the same characteristics, unlike fossil raw materials. It is for these reasons that the attention of scientists and inventors has been focused on solving one of the key problems facing modern science for many years – the direct oxidation of atmospheric nitrogen. Under natural conditions, direct oxidation of atmospheric nitrogen into nitrogen oxides occurs during a thunderstorm in lightning discharges, as well as in the upper layers of the atmosphere under the influence of solar radiation, namely its ultraviolet section.

In work [1], the process of direct oxidation of atmospheric nitrogen with the formation of nitrous oxide through the interaction of products of thermal decomposition of hydrogen peroxide with atmospheric nitrogen at a temperature of approximately 800 K (known as the Nagiyev method) was theoretically substantiated and experimentally implemented. The disadvantage of this method is its limited distribution. This is because, firstly, nitrous oxide is, in fact, as inert as atmospheric nitrogen, and, secondly, nitrous oxide itself is not an acid-forming oxide.

Works [2, 3] show that the Karavaev method is the most promising for the industrial implementation of the process of direct oxidation of atmospheric nitrogen. This method is based on the unique properties of nitric acid and makes it possible to achieve up to 60 % increase in the formation of nitrogen oxides. However, the disadvantage is that the process takes place at a temperature of about 1050 K, has a limited temperature range to carry out, and requires a complex hardware design. It is precisely because of these limitations that this method has not been widely used on an industrial scale in the last few decades.

In work [4], the production of nitric acid by direct oxidation of atmospheric nitrogen in the presence of hydrogen peroxide and nitric acid (Zakharov method) was theoretically proven. However, the disadvantage is the complexity of technical implementation. Therefore, there is no successful implementation of this method, even under laboratory conditions, yet.

In the experiments [5], the only currently reliably functioning method of obtaining nitrogen oxides through the catalytic oxidation of ammonia is considered in detail. This method uses natural gas to bind atmospheric nitrogen, which actually becomes a cost object in the process of producing nitric acid. However, an important drawback is the large amount of greenhouse gases released during the production of nitric acid, and the significant energy consumption of the process. This ultimately leads to a significant increase in the cost of produced nitric acid.

In work [6], studies of the direct reaction of ammonia oxidation to nitrogen oxide indicate that the reaction products are formed through an extremely fast, highly exothermic,

and non-equilibrium process that occurs according to a defined complex mechanism. The efficiency of NO formation depends significantly on high temperature, approximately in the range of 1100–1300 K, and elevated pressure. The disadvantage is that this high-temperature catalytic process of ammonia oxidation can cause mechanical damage to the catalytic grids, the formation of platinum oxides on the catalyst surface (due to insufficient mixing of ammonia and air), and uneven gas distribution over the catalyst surface.

In [7], a traditional method is shown, which is effective, but the overall performance is limited by several disadvantages. The first drawback is that approximately 30 % of the total cost of producing nitric acid is ammonia as a feedstock, which limits the economic output from this feedstock source and includes environmental concerns. Another disadvantage is the loss of platinum group metals through evaporation and erosion. Another limitation is the complex process of condensate formation during the formation of HNO<sub>3</sub> and the high capital investment and operating costs for numerous operation units.

In [8], researchers claim that the injection of nitric acid into the atmosphere at a temperature of 758–1173 K leads to an increase in nitrogen oxides by 60 %. This gives reason to assume that radicals capable of activating and oxidizing molecular nitrogen can be formed in the products of thermolysis of nitric acid. The results of the study indicate that such high-energy compounds in the products of rapid thermolysis of nitric acid can be oxo-isomers. Therefore, the obtained conclusions are a logical explanation of the experiments carried out in [9] within the limits of the autocatalytic use of nitric acid vapors for the activation of molecular nitrogen. However, these studies did not find further development.

All this gives reason to assert that it is expedient to carry out research aimed at the direct oxidation of atmospheric nitrogen in order to obtain nitric acid, which is important and relevant. The results of the research could become a starting point for the development of new methods of atmospheric nitrogen binding and methane activation, which are fundamental tasks in the field of chemical science and technology.

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## 3. The aim and objectives of the study

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The purpose of our work is to determine the possibility of using cold plasma to create conditions for the oxidation of atmospheric nitrogen. This will make it possible to implement the process of oxidizing atmospheric nitrogen into nitrogen oxides in a cold plasma flow.

To achieve the goal, it is necessary to solve the following tasks:

- to investigate the effectiveness of using cold plasma to oxidize atmospheric nitrogen;
- to investigate the effect of nitric acid, hydrogen peroxide, alcohols as activators of atmospheric nitrogen oxidation in a high-energy field.

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## 4. The study materials and methods

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### 4.1. The object and hypothesis of the study

The object of research is the process of oxidation of atmospheric nitrogen into nitrogen oxides.

The subject of research is the oxidation of atmospheric nitrogen into nitrogen oxides.

The prerequisites of the proposed process are as follows. In the laboratory, atomic nitrogen can be obtained using a high-frequency electric discharge. Atomic nitrogen shows much higher activity compared to atmospheric nitrogen. This type of nitrogen can interact with sulfur, phosphorus, arsenic, as well as with various metals, such as lithium, magnesium, mercury, and others.

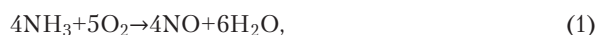
Even at temperatures exceeding 3300 K, the level of thermal dissociation of  $N_2$  is only 0.1 %. At temperatures above 5300 K, this level increases to a few percent at atmospheric pressure.

It should be noted that nitrogen oxides are also formed during electrical discharges, for example, in a lightning discharge.

Nitrogen monoxide is oxidized to nitrogen dioxide in the presence of oxygen under any conditions.

The production of nitric acid is important for the production of nitrate-containing compounds such as urea, ammonia, sodium, and potassium nitrates, etc. Most modern industries, including Ukrainian ones, obtain nitric acid by oxidizing ammonia and further absorbing nitrogen oxides. This process is characterized by the use of large amounts of methane and energy for the synthesis of ammonia, as well as environmental problems related to the treatment of tail gases.

The conventional industrial process for the production of nitric acid involves the catalytic combustion of ammonia over a platinum-rhodium alloy catalyst (95 % Pt and 5 % Rh), which is a knitted lattice. This occurs at temperatures of 1100–1300 K and pressure of 0.4–1 MPa in the catalytic chamber. Nitrous oxide (NO) is produced during this process. Further oxidation of nitrogen oxide occurs at a temperature of the order of 330 K and increased pressure in the oxidation chamber, forming nitrogen dioxide ( $NO_2$ ), which is then combined with water in the absorption column to obtain nitric acid:

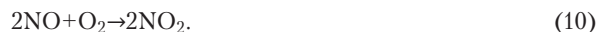
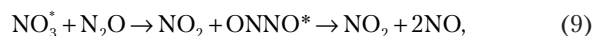
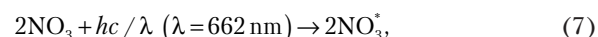
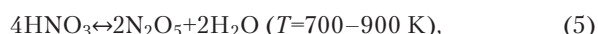


During this process,  $N_2O$  is also formed as a non-selective reaction product, according to equation (4):



The process of oxidation of molecular nitrogen ( $N_2$ ) by high-energy oxidants, such as nitric acid vapor ( $HNO_3$ ) and its thermolysis products – the Karavaev effect, and hydrogen peroxide ( $H_2O_2$ ) and its decomposition products – the Nagiev effect, can lead to the formation of various nitrate-containing compounds, such as nitrogen oxides ( $NO_x$ ) and nitrates ( $NO_3^-$ ).

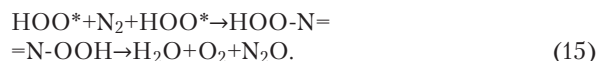
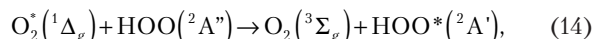
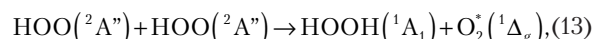
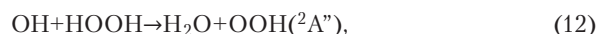
Nitric acid ( $HNO_3$ ) has high reactivity and can be used to oxidize atmospheric nitrogen. Nitrogen oxides ( $NO_x$ ) are formed during these reactions. Thermolysis of nitric acid ( $HNO_3$ ) when heated to temperatures of the order of 1000 K occurs according to the reaction:



Different techniques and analytical tools are used to study the reactivity of nitric acid and its decomposition products in the process of atmospheric nitrogen oxidation.

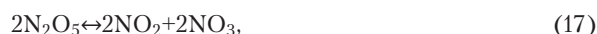
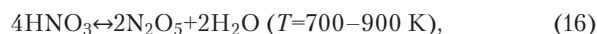
One method involves determining the concentration of  $NO_x$  in the atmosphere by using analytical tools such as gas chromatography and mass spectroscopy. These methods make it possible to determine the amount of  $NO_x$  and other compounds produced.

Oxidation of molecular nitrogen can proceed in different reaction ways depending on the conditions and the oxidants used. The Nagiyev effect showed the possibility of binding atmospheric nitrogen by products of thermal decomposition (temperature of the order of 900 K) of hydrogen peroxide ( $H_2O_2$ ):



The formed nitrate-containing compounds, such as nitrogen oxides and nitrates, can have a significant impact on the chemical composition of the atmosphere. For example, nitrogen oxides ( $NO_x$ ), especially nitrogen dioxide ( $NO_2$ ), can contribute to the formation of smog and acid rain, as well as affect air quality and human health. Nitrates can be important sources of nitrate-containing ions for plants in the process of nitrification. These processes are complex and depend on many factors, such as temperature, pressure, reactant concentrations, and the presence of catalysts.

The analysis of the results of quantum-chemical calculations and experimental studies of the Karavaev and Nagiev effects made it possible to propose a scheme using a compatible process of oxidation of molecular nitrogen by products of thermal decomposition of nitric acid and products of thermal decomposition of hydrogen peroxide (Zakharov method):



The proposed method for obtaining nitric acid consists of several stages:

- thermal destruction of  $\text{HNO}_3$  – reaction (18);
- dissociation of  $\text{N}_2\text{O}_5$  with the formation of  $\text{NO}_3$  trioxide – reaction (17);
- photochemical activation of trioxide in the excited state (reaction 20);
- activation of molecular nitrogen and nitrous oxide as a product of destruction (reactions 20 and 21);
- chemical reactions of nitric acid reproduction – reactions (22), (23).

By analogy with the nitrogen molecule, the alkane molecules are also inert in a wide range of temperatures. Works [9, 10] show the possibility of effective activation of alkane molecules in high-energy cavitation and electromagnetic fields. Given that the C–C and C–H bond energy in alkane molecules is much lower than the bond energy in a nitrogen molecule, it is promising to use high-energy electromagnetic fields (plasma of all types, electric discharges, etc.).

#### 4. 2. Justification of the choice of research methods

The introduction of the technology for obtaining nitric acid according to the Zakharov method, which allows obtaining this product without the use of ammonia through the stage of natural gas conversion, has the potential to reduce emissions of carbon oxides and heat into the environment. This will contribute to a significant improvement in the environmental indicators of production. To implement this technology, it is necessary to conduct a process of direct oxidation of atmospheric nitrogen into nitrogen oxides. In the course of research, the process of atmospheric nitrogen oxidation in cold plasma with the participation of activator substances was studied. Therefore, a laboratory facility for obtaining nitrogen oxides by direct oxidation of atmospheric nitrogen in a cold plasma flow was developed. Based on the results of quantum-chemical calculations using the Zakharov method and experimental studies of the Karavaev and Nagiev effects, a scheme for using the process of molecular nitrogen oxidation by using products of thermal decomposition of nitric acid and hydrogen peroxide is proposed. It was found that conditions close to normal show a low efficiency of conversion of atmospheric nitrogen into nitrogen dioxide and nitric acid, amounting to thousandths of a percent. An attempt to introduce these processes into the field of high-energy cold plasma is proposed.

Among the modern technical devices that are mass-produced, provide stable operation, and are capable of forming a high-energy field for the oxidation of atmospheric nitrogen, plasma torches and a Tesla coil should be singled out. In this work, it is proposed to use the Horynich plasma torch as a source of plasma generation for the construction of laboratory installations in order to compare the effectiveness of using different conditions of plasma formation and the effectiveness of various activator substances. This device has the ability to adjust the voltage and current. Nitric acid plants under development must meet several key principles:

- creating a concentration of activated particles  $\text{NO}_3^*$  (ensures the implementation of reactions (1) to (3));
- creating a concentration of activated OH particles (ensures the implementation of reaction (12));
- the possibility of bringing  $\lambda=662$  nm irradiation to the reaction zone;
- the presence of nitrogen oxides  $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$  in the reaction zone.

These principles can be implemented by various technical solutions. It is most expedient to check the viability of such

technical solutions by changing options for the design of the installation.

#### 4. 3. Laboratory setup and conditions for conducting experiments

It is proposed to make a reactor in the form of a tube made of a heat-resistant material (quartz glass or other material, for example, titanium) and supply it with a plasma with a temperature of more than 3000 K. This will allow creating a number of activated particles in the air stream fed through the quartz tube, among which it is guaranteed oxides of nitrogen will be present. Water vapor in the air is theoretically able to generate OH radicals. Such a technical solution makes it possible to implement the key principles provided that lighting is provided by the appropriate device. To check the technical solutions (individually or their combinations), various versions of the installation design were created. The possibility of carrying out a continuous process was checked for such a period of time, which would allow it to be possible to obtain nitric acid of a certain concentration as a product.

The main elements of the installation design (Fig. 1) are a node for generating activated particles (this is solved with the help of a plasma generator), a reactor, an absorber-reoxidizer of nitrogen oxides.

Analysis of reaction products should be carried out in the following ways:

- 1) analysis of nitrogen oxides NO,  $\text{NO}_2$  in the range from zero to 2000 ppm – with the help of a gas analyzer OXI-5M-5N;
- 2) analysis of oxygen, nitrogen, all known nitrogen oxides – NO,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$  – in the range from zero to 10 % vol. – with the help of a gas chromatograph;
- 3) analysis of the aqueous solution for the concentration of nitrate ions – using the AI-125 ionometer.

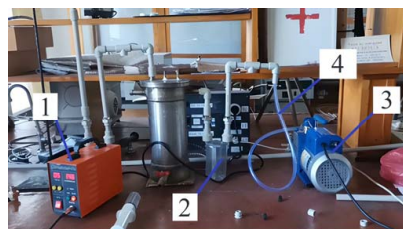


Fig. 1. Photograph of the installation for obtaining nitrogen oxides by direct oxidation of atmospheric nitrogen in a cold plasma stream: 1 – plasma generator control unit; 2 – buffer; 3 – vacuum pump; 4 – output of products

Installations can work either under discharge – air movement is provided by a vacuum pump, or under air pressure supplied by a compressor. The measurement of air flow is carried out by measuring the volume of gases collected in the storage tank for a certain period of time in a steady state and the corresponding conversion to volume velocity.

The installation (Fig. 2) consists of the main modules: a plasma generator, a reactor part, a module for fixing nitrogen oxides.

The elements of the plasma generator PG that are important for the process of producing nitric acid are the liquid dosing unit E1, which, upon entering the discharge zone, generates active particles – radicals, ions, atoms, etc. Such a liquid can be water, monoatomic alcohols, ethers, hydrogen peroxide, nitric acid. The creation of a discharge on the cathode and dosing of liquid occurs through the dosing device F,

and its design depends on the length and strength of the discharge, the amount of liquid supplied to the plasma field. The dosing device F is a consumable and is periodically replaced either completely or in part of the cathode.

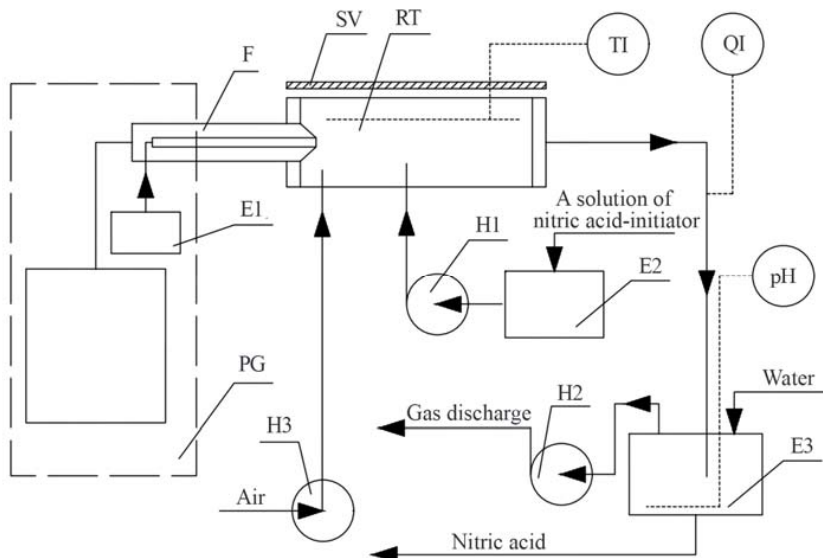


Fig. 2. Installation for obtaining nitric acid through the controlled activation of atmospheric nitrogen with the generation of activated particles by a plasma generator

The reactor assembly RT is a quartz tube, on one side of which a plasma discharge enters, in which ionization and thermal dissociation of the activator substance takes place. Air enters the reactor through a separate opening, and its flow rate is regulated by changing the pressure at the inlet to the H2 vacuum pump.

The quartz tube is illuminated by a special SV lamp that generates light waves with a length of  $662 \pm 10$  nm. It is the waves of this length that activate nitrogen oxides and contribute to the formation of nitrogen oxide (II).

There is also a separate unit for dosing water into the reactor zone, consisting of pump H1 and tank E2. This water is needed under some operating modes of the plant to quickly reduce the temperature in the reaction zone. This pump can also dose a solution of activator substances (nitric acid or hydrogen peroxide solution), which enter the plasma zone and generate activated particles that are initiators of the direct synthesis of nitrogen oxides from atmospheric nitrogen.

Temperature control along the length of the reactor is carried out using a TI pyrometer, and temperature regulation can occur by changing the amount of air and the speed of air movement through the reactor.

The concentration of nitrogen oxides in the air after the reactor is measured by a QI chromatograph operating under continuous mode or by an OXI-5M-5N gas analyzer. Thus, at the installation, there is an opportunity to influence the composition of products within the framework of one experiment by changing the amount of the activator substance, the temperature regime in the reactor, and the intensity of reactor irradiation. Nitrogen oxide (II) is oxidized to nitrogen oxide (IV) at room temperature and absorbed in absorber E3 with the formation of nitric acid. The efficiency of the process is additionally evaluated by changing the pH of the solution in the absorbers using a pH meter.

The movement of air through the installation is carried out either by a H2 vacuum pump and a RT reactor (at the same time, the pressure in the installation is lower than atmospheric). At the same time, the air gets into the installation tract through leaks between the nozzle F or the compressor H3, and then the pressure in the installation is higher than atmospheric.

For conducting laboratory studies, the installation shown in Fig. 1 was selected. The parameters of the plasma generator were set for reasons of formation of a stable plasma flow. For the selected plasma torch model, they are: current strength – 8.0 A, voltage – 170 V. Air flow is blown through the reaction volume in which the plasma flow is stably formed. Air consumption varied in the range from 0 to 3000 l/h. Distillate and liquid activators are used as the liquid whose vapor forms the plasma. The distillate tank, pipelines, and materials of the plasma torch are selected in such a way that they withstand the effects of acids, alcohols, and hydrogen peroxide. As activator substances, it is proposed to use liquids that are capable of forming OH radicals during thermal decomposition. In our work, ethanol and hydrogen peroxide were used as such liquids.

## 5. Results of studies of the oxidation process of molecular nitrogen in the high-energy field of a plasma torch

### 5.1. Studying the effectiveness of using cold plasma for atmospheric nitrogen oxidation

Oxidation of atmospheric nitrogen in the plasma stream, which is formed by distillate steam, was chosen as the zero experiment. Plasma generator parameters: liquid – distillate; amperage – 8.0 A; voltage 170 V.

Graphically, the dependence of the concentration of nitrogen monoxide and nitrogen oxide on the air flow through the atmospheric nitrogen oxidation installation is shown in Fig. 3.

The dependence of the concentration of nitrogen oxide (II)  $C_{NO}$  on the air flow  $V_{air}$  is described by equation (23), and the dependence of the concentration of nitrogen oxide (IV)  $C_{NO_2}$  on the air flow  $V_{air}$  is described by equation (24). Equations (23) and (24) describe the behavior of the system in the range of air flow rates 0–1400 l/h:

$$C_{NO} = 10^{-8}V_{air}^3 - 4 \cdot 10^{-5}V_{air}^2 + 0.0281V_{air} - 1.6472, \quad (23)$$

$$C_{NO_2} = -4 \cdot 10^{-8}V_{air}^3 + 0.0001 \cdot 10^{-5}V_{air}^2 + 0.1336V_{air} + 46.987. \quad (24)$$

In the current work, among the methods of mathematical statistics, only averaging was used by finding the average arithmetic value at each point of the experiment. In total, three studies were conducted with five series in each. In further research, with an increase in the volume of experimental data, it will be appropriate to apply the entire apparatus of mathematical statistics to treat experimental results.

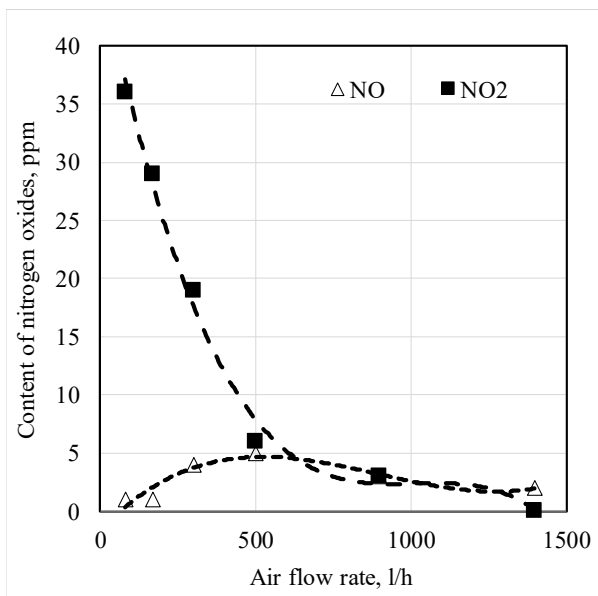


Fig. 3. Dependence of nitrogen oxide content on air flow through the unit

Analyzing the obtained dependences, it is possible to note the maximum concentration of nitrogen dioxide at the level of 5 ppm, with an air consumption through the installation of 500 l/h. With a further increase in air flow, the concentration of nitrogen dioxide decreases slightly, but is at the level of 2–3 ppm.

In the present work, a number of studies were carried out, in which the influence of the concentration of ethanol in the mixture, which was used in the formation of plasma, was determined. Experimentally, it was established that the composition of 76 % distillate and 24 % ethanol is optimal for the formation of a plasma flow. The results of the research are shown in Fig. 4.

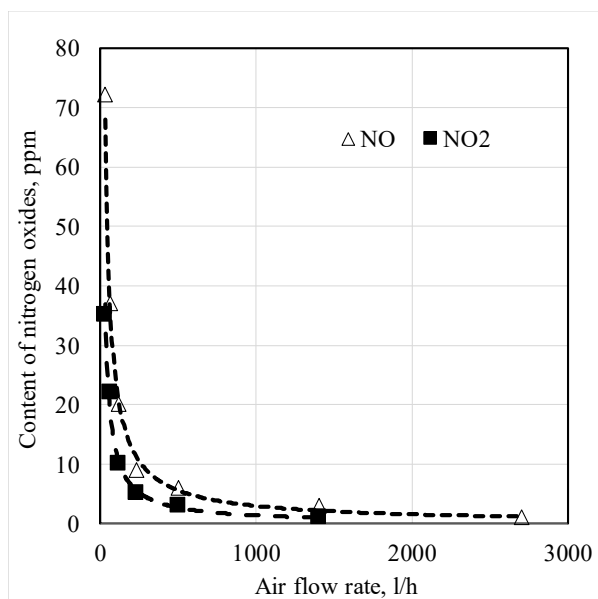


Fig. 4. Dependence of the content of nitrogen oxides on the air flow through the installation when using a mixture of 76 % distillate – 24 % ethanol to form a plasma flow

The dependence of the concentration of nitrogen oxide (II)  $C_{NO}$  on the flow of air  $V_{air}$  is described by equation (25), and the dependence of the concentration of nitrogen oxide (IV)  $C_{NO_2}$  on the flow of air  $V_{air}$  is described by equation (26). Equation (25) describes the behavior of the system in the air flow range of 0–2500 l/h, and equation (26) describes the behavior of the system in the air flow range of 0–1400 l/h:

$$C_{NO} = 1,576.1 \cdot V_{air}^{-0.91}, \quad (25)$$

$$C_{NO_2} = 992 \cdot V_{air}^{-0.95}. \quad (26)$$

Analyzing the established dependences, it can be noted that the presence of ethanol in the steam that forms the plasma flow increases the amount of nitrogen oxides by approximately 1.3 times, and the amount of nitrogen oxides formed in the reactor is almost independent of the air flow but depends only on efficiency of the radical generator.

## 5. 2. Study of the effect of nitric acid, hydrogen peroxide, and alcohols as activators of atmospheric nitrogen oxidation in a high-energy field

It is known that hydrogen peroxide forms two OH-radicals during thermal decomposition. It was established experimentally that the use of a 3 % solution of hydrogen peroxide in the distillate as a working fluid allows obtaining a stable plasma flow. The results of studies of the oxidation of atmospheric nitrogen in the plasma flow of 97 % distillate vapor – 3 % hydrogen peroxide are shown in Fig. 5.

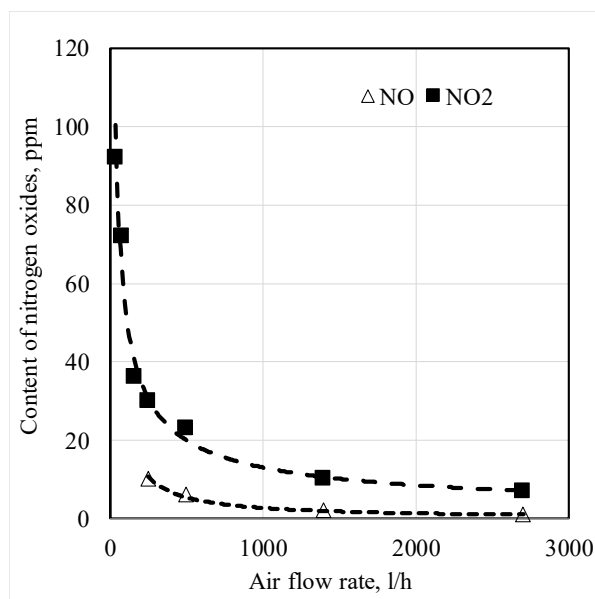


Fig. 5. Dependence of the content of nitrogen oxides on the air flow through the installation when using a mixture of 97 % distillate – 3 % hydrogen peroxide to form a plasma flow

The dependence of the concentration of nitrogen oxide (II)  $C_{NO}$  on the flow of air  $V_{air}$  is described by equation (27), and the dependence of the concentration of nitrogen oxide (IV)  $C_{NO_2}$  on the flow of air  $V_{air}$  is described by equation (28). Equation (27) describes the system behavior in the air flow range of 250–2700 l/h, and equation (28) describes the system behavior in the air flow range of 0–2700 l/h:

$$C_{NO} = 2,443 \cdot V_{air}^{-0.98}, \tag{27}$$

$$C_{NO_2} = 906.7 \cdot V_{air}^{-0.61}. \tag{28}$$

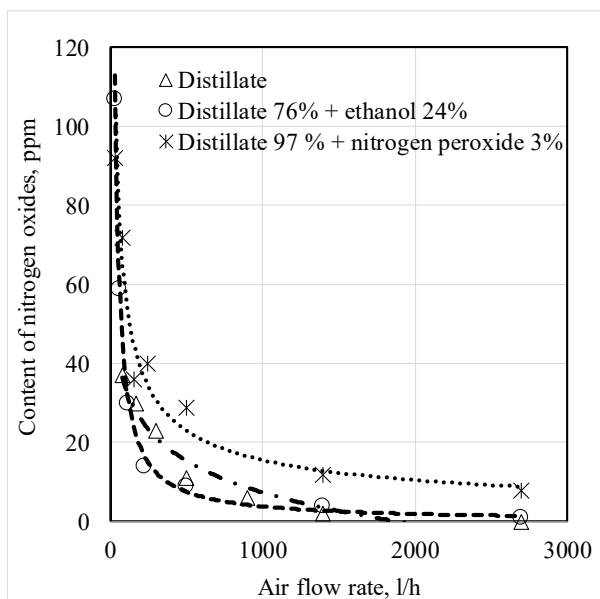


Fig. 6. Dependence of the content of nitrogen oxides on the air flow through the installation when using different activators

Fig. 6 shows the dependence of the content of nitrogen oxides  $NO_x$  on the air flow through the installation using different activators, which demonstrates that hydrogen peroxide is a much more effective source of radicals than distillate and ethanol.

The dependence of the concentration of nitrogen oxides  $NO_x$  on the air flow  $V_{air}$  during the operation of a plasma generator on distillate is described by equation (29), the dependence of nitrogen oxides  $NO_x$  on the air flow  $V_{air}$  when using 24 % ethanol as an activator is described by equation (30), and the dependence of nitrogen oxides  $NO_x$  on the air flow  $V_{air}$  when using 3 % hydrogen peroxide as an activator is described by equation (31):

$$C_{NO} = -11.57 \ln(V_{air}) + 87.3, \tag{29}$$

$$C_{NO_2} = 3,409.7 \cdot V_{air}^{-0.98}, \tag{30}$$

$$C_{NO} = 788.9 \cdot V_{air}^{-0.57}. \tag{31}$$

Chart 6 of the dependence of the content of nitrogen oxides on the air flow through the installation when using different activators demonstrate that the process of formation of nitrogen oxides in a stable plasma flow occurred in all experiments. But the highest concentration of nitrogen oxides reached was only 99 ppm.

### 6. Discussion of results of investigating the oxidation of molecular nitrogen in the plasma formed in a vapor of activator substances

The introduction of reproductive technology for obtaining nitric acid is an innovative approach that makes it

possible to produce this acid, avoiding the stage of obtaining ammonia through the conversion of natural gas.

The analysis of the results of our research confirmed the presence of the formation process of nitrogen oxides in a stable plasma flow during all experiments. The amount of nitrogen oxides turned out to be dependent on various factors, such as the parameters of the plasma generator, the composition of the liquid used in the burner, and the volume of air supply. It should be noted that the maximum achieved concentration of nitrogen oxides was limited. From our results, it can be concluded that the limiting stage of the process of oxidation of atmospheric nitrogen is the process of formation of radicals, that is, the ability of the plasma generator to create them under the given conditions (Fig. 3)

Analyzing the results of this study, it can be noted that the presence of ethanol in the steam that forms the plasma flow increases the amount of nitrogen oxides by approximately 1.3 times. The nature of the dependence allows us to say that the amount of nitrogen oxides formed in the reactor is almost independent of the air consumption but depends only on the efficiency of the radical generator.

Analysis of the results obtained in this series of studies allows us to conclude that hydrogen peroxide is a much more effective source of radicals than distillate and ethanol. The presence of even 3 % of hydrogen peroxide in the liquid that forms the plasma flow made it possible to increase the concentration of nitrogen oxides in the gases at the outlet of the installation by more than 6 times.

It is worth noting that replacing the distillate with a mixture of 76 % distillate and 24 % ethanol did not lead to a significant increase in the concentration of nitrogen oxides formed. Thus, considering ethanol as an activator of atmospheric nitrogen oxidation turns out to be ineffective (Fig. 4).

The dependences shown in Fig. 6 suggest that in each series of studies, the amount of nitrogen oxides remained almost unchanged (Tables 1, 2). Under stable conditions of operation of the plasma generator, its efficiency almost does not depend on the volume of air supplied through the system. However, it largely depends on the amount of OH- radicals formed during the decomposition of the activator substance. The analysis of our studies reveals that the process of formation of nitrogen oxides in a stable plasma flow occurred in all experiments. The content of nitrogen oxides depends on the operating parameters of the plasma generator, on the composition of the liquid filled into the burner, and on the air consumption. But the highest concentration of nitrogen oxides reached was only 99 ppm.

From the above studies, it can be concluded that the limiting stage of the atmospheric nitrogen oxidation process is the formation of radicals. In other words, the success of the plasma generator in forming them under certain conditions predetermines its performance.

The disadvantage of this study is that the attempt to obtain nitric acid by absorbing the obtained nitrogen oxides in a Drexel glass was unsuccessful. Titration methods and the use of a nitrate-selective electrode to determine the nitric acid in the beaker did not yield results. This is probably due to insufficient concentration of nitrogen oxides in the gas mixture.

The design of the proposed reactor (Fig. 2) turned out to be stable, but the bottleneck was the nozzle of the plasma generator burner. It overheated after 20–50 minutes of operation of the installation. The burner required constant refueling with liquid, which affected the concentration of nitrogen oxides, and although the process was reproduced in various parallel experiments, controlling it turned out to be difficult.

It was not possible to detect the influence of the intensity of irradiation because in this design light was a side effect accompanying the plasma generation process.

Our results of theoretical and practical studies give grounds for the assumption that under certain conditions, the process of atmospheric nitrogen oxidation can be carried out in the plasma flow. This stage is critical for obtaining nitric acid by direct oxidation of atmospheric nitrogen.

During the comparison of three activator substances, which form OH- radicals during decomposition, it was established that hydrogen peroxide is the most promising activator for the process of oxidation of atmospheric nitrogen in the plasma flow. The effect of the concentration of hydrogen peroxide in the distillate and the improvement of the experimental setup in order to ensure the uninterrupted and safe operation of the activator substance dosing unit remain the object of further research.

The results of the experiment give reason to assume that the amount of nitrogen oxides formed in the installation depends on the efficiency of creating a stable flow of OH-radicals in the plasma flow.

The current paper explores the possibilities of using cold plasma to create conditions for the oxidation of atmospheric nitrogen. And it was also determined that for the implementation of the process of obtaining nitric acid from atmospheric air by the Zakharov method using the Karavaev and Nagiyev effects, a laboratory installation based on the "Horynych" plasma generator was proposed and implemented.

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## 7. Conclusions

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1. As a result of the study, the effectiveness of using cold plasma for the oxidation of atmospheric nitrogen was established, which is confirmed by the results of experimental data. It is shown that the amount of nitrogen oxides formed in the installation depends on the efficiency of the formation of a stable flow of OH- radicals in the plasma flow. The dependence of the amount of nitrogen oxides on the parameters of the plasma generator, the composition of the liquid used in

the burner, and the volume of air supply was also revealed. It was established that the presence of ethanol in the steam that forms the plasma flow increases the amount of nitrogen oxides by approximately 1.3 times.

2. As a result of our research, the influence of nitric acid, hydrogen peroxide, alcohols as activators of the process of oxidation of atmospheric nitrogen in a high-energy field was revealed. It was determined that when comparing three activator substances, which are able to form OH- radicals during their decomposition, it is hydrogen peroxide that is the most promising activator substance for carrying out the process of atmospheric nitrogen oxidation in the plasma flow. Namely, the use of a hydrogen peroxide solution, even in the amount of 3 % in the distillate, leads to a significant, almost sixfold, increase in the concentration of nitrogen oxides formed.

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## Conflicts of interest

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The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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## Data availability

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All data are available in the main text of the manuscript.

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## Use of artificial intelligence

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The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

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