

THERMAL CONVERSION OF NITROGEN OXIDES IN A FLOW REDUCING GAS

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Air pollution, even in very low doses, seriously damages human health. Nitrogen oxides combine with water vapor in the atmosphere to form acids, which in the form of acid rain fall into the soil and acidify it. We have investigated the process of thermal decomposition of nitrogen oxides in a laboratory setup in the presence of gaseous and solid reducing agents. The possibility of sanitary neutralization of nitrogen oxides by their thermal decomposition without the use of expensive catalysts used in industry has been shown. A method and design of a reactor for the thermal decomposition of nitrogen oxides (N_xO_y) in the presence of reducing agents has been developed. The essence of the method we have developed is as follows: natural gas is burned in a reactor, and a mixture of nitrous gas with oxygen or air is used as an oxidizer for burning natural gas. The amount of natural gas supplied for combustion must be calculated so that the temperature of the gas mixture reaches 1100–1200°C and the minimum amount of oxygen remains in the gas. At this temperature, a significant part of the nitrogen oxides decomposes. After the reactor, in the presence of a solid reducing agent (coke), the final decomposition of the residual nitrogen oxides takes place. The degree of decomposition of nitrogen oxides in the first zone of the reactor in the presence of natural reducing gas is 85.0–88.7%, and in the second zone in the presence of a reducing agent-coke is 97.4–99.5%. The concentration of nitrogen oxides at the outlet of the laboratory installation does not exceed 0.02–0.05%. To achieve the above indicators, the following technological regime must be observed: temperature in I and II zones – 1000 °C, combustion gas consumption – 3–4% of the total volume of gas and air supplied for combustion, coke consumption 0.25 kg per 1 kg of oxides nitrogen entering the second zone of the reactor. *Key words:* air pollution, nitrogen oxides, thermal method, degree of purification.

Термічна конверсія оксидів азоту у потоку газу-відновника. Кузнєцов С.І., Малєєв В.О., Семенченко О.О., Безпальченко В.М.

Забруднення повітря навіть у малих дозах завдає серйозної шкоди здоров'ю людей. Оксиди азоту, з'єднуючись в атмосфері із парами води, утворюють кислоти, які у вигляді кислотних дощів потрапляють у ґрунт та закислюють його. Нами досліджено процес термічного розкладання оксидів азоту на лабораторній установці у присутності газоподібних та твердих відновників. Показано можливість санітарного знешкодження оксидів азоту шляхом їх термічного розкладання без застосування коштовних каталізаторів, що використовуються у промисловості. Розроблено метод та конструкцію реактора для термічного розкладання оксидів азоту (N_xO_y) у присутності відновників. Сутність розробленого методу: у реакторі спалюється природний газ; у якості окислювача для спалювання природного газу застосовують суміш нітрозного газу з киснем або повітря. Кількість газу, що подається на спалювання, розраховується таким чином, щоб температура газової суміші досягала 1100–1200°C і в газі залишалася мінімальна кількість кисню. За цієї температури відбувається розкладання значної частини оксидів азоту. Після реактора у присутності твердого відновника (коксу) відбувається остаточне розкладання залишків оксидів азоту. Ступінь розкладання оксидів азоту у першій зоні реактора у присутності газу-відновника (метан) становить 85,0–88,7%, у другій зоні у присутності коксу – 97,4–99,5%. Концентрація оксидів азоту на виході лабораторної установки становить 0,02–0,05%. Для досягнення наведених показників необхідно дотримуватися такого технологічного режиму: температура в I та II зоні – 1000 °C; витрата пального газу – 3–4% від повного обсягу газу та повітря, що подається на згоряння; витрата коксу – 0,25 кг на 1 кг оксидів азоту, що надходять у другу зону реактора. *Ключові слова:* забруднення атмосферного повітря, оксиди азоту, термічний метод, ступінь очищення.

Formulation of the problem. Air pollution, even in very small doses can bring serious harm to human health [1]. On air pollution, in particular, suffer breathing human organs. Nitrogen oxides, combining with water vapor in the atmosphere, form acids, which in the form of acid rain fall into the soil and acidify it [2]. Restoring fertility acidified soils requires great costs. Acid rain also has a negative impact on water bodies (lakes, rivers, bays, ponds). This process increases the acidity of water to a level at which flora and fauna die [3]. The bulk of man-made pollution is formed when organic fuel is burned. A significant part of these pollutants is accounted for by nitrogen oxides [4]. The neutralization of these emissions is a very urgent task.

Analysis of recent research and publications.

There are various methods for cleaning gases from nitrogen oxides. Some of them have been introduced into production, others are under development and laboratory testing. The purification of waste gases from nitrogen oxides is based on oxidation, reduction and sorption processes. Oxidative methods are based on the preliminary oxidation of NO to N_2O_3 and NO_2 followed by the absorption of oxidized nitrous gases by various sorbents [5,6]. Reduction methods are based on catalytic or thermal reduction of oxides to neutral substances. A wide variety of methods is associated with various technological processes in which nitrous gases

are released into the atmosphere. These emissions differ in the number, content of nitrogen oxides, NO oxidation, oxygen and other impurities, temperature and other characteristics. There are optimal treatment methods for different emissions [7, 8]. At a high (more than 3%) oxygen content in the purified gas, it is advisable to use thermal reduction. The most effective issue of neutralizing nitrogen oxides is solved in the production of nitric acid [9]. For this – of the process was developed and implemented a method of catalytic gas cleaning over a palladium catalyst. Nevertheless, of the catalytic – cue method associated with the installation of sophisticated equipment and the use of expensive catalyst [10]. The catalytic method of decomposition of nitrogen oxides is advisable for gases containing no more than 1% NO₂ and up to 4–5% oxygen. In addition, catalysis

is effective at high pressures. In industry there are a large number of sources emitting nitrous gas into the atmosphere, containing up to 3–5% nitrogen oxides and up to 10–20% oxygen. These systems include off-gases from the production of oxalic acid, which contain 2.0-2.5% nitrogen oxides and about 10% oxygen [11]. The catalytic method of neutralization is unacceptable for such systems. Other well-known methods, for example, alkaline ones, which are bulky and have a low degree of purification (about 60–70%), also turn out to be ineffective under these conditions. Currently, the question of neutralizing nitrogen oxides in the production of oxalic acid remains open.

The purpose of the research was to develop a method for the thermal decomposition of nitrogen oxides, which ensures the purification of waste gases to maximum permissible concentrations.

Main material. A method and design of a reactor for the thermal decomposition of nitrogen oxides (N_xO_y) in the presence of reducing agents has been developed .

The essence of the method we have developed is as follows: natural gas is burned in the reactor (first zone), and a mixture of nitrous gas with oxygen or air is used as an oxidizer for burning natural gas. The amount of natural gas supplied for combustion must be calculated so that the temperature of the gas mixture reaches 1100–1200°C and the minimum amount of oxygen remains in the gas. At this temperature, a significant part of the nitrogen oxides decomposes. Further, the gas mixture enters the second zone, where the decomposition of residual nitrogen oxides occurs in the presence of a solid reducing agent – coke.

To test the working hypothesis of the developed method of thermal decomposition of nitrogen oxides, a laboratory pilot installation was made, the diagram of which is shown in fig. 1.

The reactor for thermal decomposition of nitrogen oxides 7 is made of quartz glass. It consists of two zones: in the first zone, the gas mixture is heated and nitrogen oxides are reduced in the presence of a gaseous reducing agent 13; in the second zone, nitrogen oxides are reduced in the presence of a solid reducing agent – coke 8. The reactor has a nozzle 14 for burning combustible gas and a connection for supplying air and nitrous gas. The installation is equipped with rotameters 1–5 for measuring

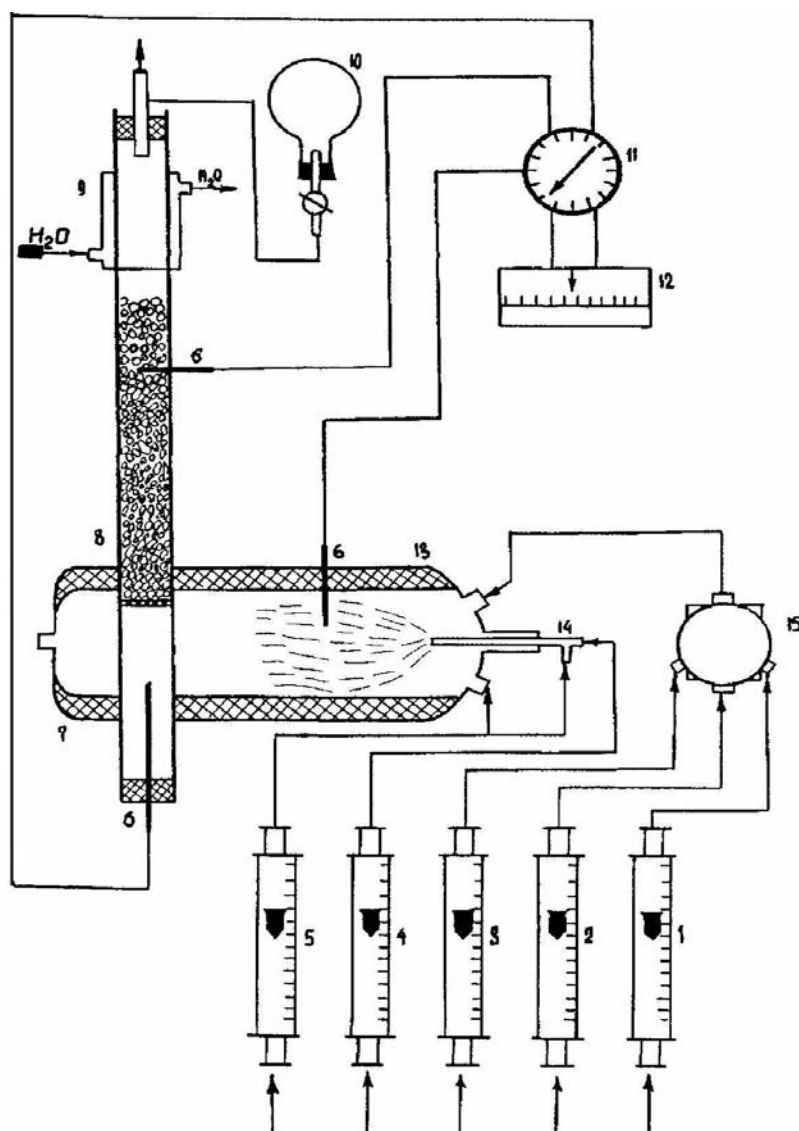


Fig. 1. Laboratory installation for thermal decomposition of nitrogen oxides
 1 – rotameter (for NO), 2 – rotameter (for N₂), 3, 5 – rotameters (for air),
 4 – rotameter (for CH₄), 6 – thermocouple, 7 – reactor, 8 – layer coke,
 9 – heat exchanger, 10 – flask, 11, 12 – thermometers,
 13 – primary reaction zone, 14 – nozzle, 15 – mixer

the flow rates of individual components of the gas mixture and thermocouples 6 with devices 11, 12 for measuring the temperature at various points of the reactor. In addition, a gas mixer 15, a heat exchanger 9 and a sampling point for gas analysis 10 are set in the installation.

Experimental technique. Air, nitrogen and nitrous gas were mixed in a certain proportion in the mixer 15 and fed into the reactor. Natural gas is also supplied here through the nozzle 14. As a result of natural gas combustion, the temperature in the first zone rises to 1100–1200 °C. The concentration of nitrogen oxides at the inlet was determined by calculation by the number of dosed components. The second zone of the reactor 8 is loaded with coke. Hot gases passing through the second zone interact with coke, resulting in the decomposition of residual nitrogen oxides. The concentration of nitrogen oxides at the outlet was determined by the method of evacuated flasks. The degree of decomposition of nitrogen oxides was determined from the content of nitrogen oxides at the inlet and outlet.

The optimal technological mode of the process of thermal decomposition of nitrogen oxides, namely the consumption of combustible gas, temperature, the amount of solid reducing agent, and the volumetric velocity of gases, has been established experimentally. To reach a temperature of 1100°C, a mixture of the following composition was fed into the reactor: air – 2.22 m³/h (94%), methane – 0.082 m³/h (3.61%), nitrogen oxides – 0.04 m³/h (1.99%). Total – 2,351 m³/h (100%). After achieving stable operation of the reactor,

the concentration of nitrogen oxides at the outlet was determined. Since the research was carried out in relation to waste gases from the production of oxalic acid, the content of oxides in them was maintained at the level of 2.0–2.5%. To achieve such a percentage of nitrogen oxides in the gas mixture, 46 dm³/h NO was supplied to the unit. The consumption of other components was controlled so that the temperature in the reactor did not drop below 1000–1100°C. In this case, a minimum amount of oxygen was supplied to the reactor, since its presence in the gas is associated with the occurrence of a side reaction $C + O_2 = CO_2 + Q$ which entails additional consumption of coke.

It should be noted that the ratio between the components adopted by us ensures the achievement of the specified temperature. An increase or decrease in the consumption of components at a constant consumption of the combustible gas leads to a decrease in the temperature in the reactor and, consequently, to a violation of the operating mode of the installation. The results of studies on the thermal decomposition of nitrogen oxides in the first zone of the laboratory unit are shown in table 1.

From the data in the table it can be seen that the degree of decomposition of nitrogen oxides at their initial concentration in the gas mixture of 2.0–2.2% is 85.0–88.7%. Subsequently, this gas is directed to the second zone of the reactor, where there is a complete decomposition of nitrogen oxides in the presence of a solid reducing agent – coke (table 2).

Table 1

Thermal decomposition of nitrogen oxides in the first zone of the reactor

Test number	Gas consumption, m ³ /h	The concentration of nitrogen oxides in the gas mixture, %		Decomposition of nitrogen oxides, %	Temperature, °C
		entrance	exit		
1	2.35	2.0	0.30	85.0	1000
2	2.35	2.1	0.305	85.5	1000
3	2.35	2.1	2.29	86.0	1000
4	2.35	2.05	2.295	85.6	1000
5	2.35	2.1	2.29	86.2	1000
6	2.35	2.2	2.29	86.8	1000
7	2.35	2.2	2.25	88.7	1000
8	2.35	2.18	2.25	88.5	1000

Table 2

Data on the decomposition of nitrogen oxides in the second zone of the reactor

№ test	Gas consumption, m ³ /h	The concentration of nitrogen oxides in the gas mixture, %		Decomposition in the second zone, %	Temperature, °C	General degree of decomposition, %
		entrance	exit			
1	2.35	0.300	0.01	96.6	1000	99.5
2	2.35	0.305	0.05	98.3	1000	97.4
3	2.35	2.290	0.03	90.0	1000	98.3
4	2.35	2.295	0.01	96.5	1000	99.5
5	2.35	2.290	0.01	96.5	1000	98.5
6	2.35	2.290	0.04	86.0	1000	98.0
7	2.35	2.250	0.01	92.0	1000	99.3
8	2.35	2.250	0.02	92.0	1000	99.2

From the data in table 2 it can be seen that the degree of decomposition of nitrogen oxides in the second zone is 97.4–99.5%. The specific consumption of coke was 0.25 kg per 1 kg of nitrogen oxides entering the second zone. The concentration of nitrogen oxides at the outlet of the laboratory installation does not exceed 0.02–0.05%.

Main conclusions. We have investigated the process of thermal decomposition of nitrogen oxides in a laboratory setup in the presence of gaseous and solid reducing agents. The degree of decomposition of nitrogen oxides in the first zone of the reactor in the presence of a reducing agent-natural gas is 85.0–88.7%, and in the second zone in the presence of a reducing agent-coke – 97.4–99.5%. The concentration of nitrogen oxides at the outlet of the laboratory installation does not exceed 0.02–0.05%. To achieve the above indicators,

the following technological regime must be observed: temperature in I and II zones – 1000 °C, combustion gas consumption – 3–4% of the total volume of gas and air supplied for combustion, coke consumption 0.25 kg per 1 kg of oxides nitrogen entering the second zone of the reactor. The possibility of sanitary neutralization of nitrogen oxides by their thermal decomposition without the use of expensive catalysts used in industry is shown.

Prospects for the use of research results. Investigations carried out in laboratory conditions have shown the high efficiency of the method of thermal decomposition of nitrogen oxides in the neutralization of concentrated nitrous gases. The next stage of research will be the verification of the developed method in industrial conditions, for example, for cleaning the entire volume of waste gas in the production of oxalic acid.

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