

S. I. KUZNIETSOV

Candidate of Technical Sciences,
Associate Professor at the Department of General Educational Humanities and Natural Sciences
Sections of Chemistry, Ecology and Life Safety
Kherson National Technical University
ORCID: 0000-0003-1766-931 X

O. A. VENHER

Candidate of Technical Sciences, Associate Professor,
Acting Head of the Department of General Educational Humanities
and Natural Sciences
Kherson National Technical University
ORCID: 0000-0002-0065-0375

V. M. BEZPALCHENKO

Candidate of Chemical Sciences, Associate Professor,
Associate Professor at the Department of General Educational Humanities and Natural Sciences
Sections of Chemistry, Ecology and Life Safety
Kherson National Technical University
ORCID: 0000-0002-1355-7938

O. O. SEMENCHENKO

Candidate of Technical Sciences, Associate Professor,
Associate Professor at the Department of General Educational Humanities and Natural Sciences
Sections of Chemistry, Ecology and Life Safety
Kherson National Technical University
ORCID: 0000-0002-1251-2711

E. S. IVKINA

Student at the Faculty of Information Technologies and Design
Kherson National Technical University

OXIDATION OF NITROGEN OXIDES BY OXYGEN IN THE LIQUID PHASE

Atmospheric air pollution ranks first in the degree of chemical danger to humans. Nitrogen oxides are among the most common and dangerous air pollutants on our planet. Waste gases, which include nitrogen oxides, are produced in a number of chemical industry productions, in oil refining processes, and during fuel combustion. The sources of waste gas emissions differ in their content of nitrogen oxides and other impurities, the degree of oxidation of nitrogen (II) oxide, temperature and pressure. Oxidation methods of sanitary purification of waste gases from nitrogen oxides based on preliminary oxidation of nitrogen (II) oxide with subsequent absorption of nitrogen (IV) and nitrogen (III) oxides (NO_2 , N_2O_3) by various absorbers are described in the work. The rate of oxidation of nitrogen (II) oxide is the limiting stage of the overall process to nitrogen (IV) oxide. Since this reaction takes place in the gas phase, absorption devices must have a fairly large free volume, so the absorption process is carried out in multi-stage packed or plate columns. In experiments on the absorption of nitrogen oxides by various liquid absorbers, the degree of absorption was 80–90%. In the process of absorption, nitrogen oxides are oxidized not only in the gas phase, but also in the liquid phase. Research was directed to the intensification of the process of oxidation of nitrogen (II) oxide in the liquid phase. The paper compares the results of studies on the rate of NO oxidation in the gas and liquid phases. The principle of oxidation in the liquid phase is included in the development of an absorption unit for the production of nitric acid. It has been proven that the intensification of the process of absorption of nitrogen oxides is possible by increasing the proportion of NO that is oxidized in the liquid phase. This is achieved by saturating the working solution with oxygen.

Key words: purification of waste gases, oxidation of nitrogen oxides.

С. І. КУЗНЕЦОВ

кандидат технічних наук,
доцент кафедри загальноосвітніх гуманітарних
та природничих дисциплін
секції хімії, екології та безпеки життєдіяльності
Херсонський національний технічний університет
ORCID: 0000-0003-1766-931X

О. О. ВЕНГЕР

кандидат технічних наук, доцент,
в.о. кафедри загальноосвітніх гуманітарних та природничих дисциплін
Херсонський національний технічний університет
ORCID: 0000-0002-0065-0375

В. М. БЕЗПАЛЬЧЕНКО

кандидат хімічних наук, доцент,
доцент кафедри загальноосвітніх гуманітарних
та природничих дисциплін
секції хімії, екології та безпеки життєдіяльності
Херсонський національний технічний університет
ORCID: 0000-0002-1355-7938

О. О. СЕМЕНЧЕНКО

кандидат технічних наук, доцент,
доцент кафедри загальноосвітніх гуманітарних
та природничих дисциплін
секції хімії, екології та безпеки життєдіяльності
Херсонський національний технічний університет
ORCID: 0000-0002-1251-2711

Є. С. ІВКІНА

студентка факультету інформаційних технологій та дизайну
Херсонський національний технічний університет

ОКИСНЕННЯ ОКСИДІВ НІТРОГЕНУ КИСНЕМ В РІДКІЙ ФАЗІ

Забруднення атмосферного повітря за ступенем хімічної небезпеки для людини посідає перше місце. Оксиди нітрогену входять до числа найпоширеніших і небезпечних забруднювачів повітря на нашій планеті. Відхідні гази, до складу яких входять оксиди нітрогену, утворюються у ряді виробництв хімічної промисловості, в процесах нафтопереробки, при спалюванні будь якого типу палива. Джерела викидів газів відрізняються за вмістом в них оксидів нітрогену та інших домішок, ступенем окиснення оксиду нітрогену (II), температурою, тиском. В роботі описано окисні методи санітарної очистки відхідних газів від оксидів нітрогену, що засновані на попередньому окисненні оксиду нітрогену (II) з подальшим поглинанням оксидів нітрогену (IV) та (III) (NO_2 , N_2O_3) різними поглиначами. Стадія, що лімітує сумарний процес, є швидкість окиснення оксиду нітрогену (II) до оксиду нітрогену (IV). Оскільки ця реакція протікає в газовій фазі, абсорбційні апарати повинні мати досить великий вільний об'єм, тому процес абсорбції проводять у багатоступінчастих насаджених або тарілчастих колонах. В досліджах по абсорбції оксидів нітрогену різними рідкими поглиначами ступінь абсорбції становила 80–90%. В процесі абсорбції відбувається окиснення оксидів нітрогену не тільки в газовій, але й в рідкій фазі. Дослідження були направлені на інтенсифікацію процесу окиснення оксиду нітрогену (II) в рідкій фазі. В роботі порівняно результати досліджень за швидкістю окиснення NO в газовій і рідкій фазах. Принцип окиснення в рідкій фазі покладено в розробку абсорбційного агрегату для виробництва нітратної кислоти. Доведено, що інтенсифікація процесу абсорбції оксидів нітрогену можлива шляхом збільшення частки NO, що окиснюється в рідкій фазі. Це досягається насиченням робочого розчину киснем.

Ключові слова: очищення відхідних газів, окиснення оксидів нітрогену.

Statement of the problem

The intensive development of industry leads to continuously increasing emissions of pollutants into the atmosphere. The total volume of industrial, agricultural and municipal waste on the scale of the entire planet per year is currently estimated at billions of tons. Various chemical substances contained in waste, entering the soil, air or water, pass through ecological links from one chain to another, eventually entering the human body. Depending on their nature, concentration, time of action on the human body, they can cause various adverse consequences. Short-term exposure to small concentrations of such substances can cause dizziness, nausea, heartburn, and cough. For example, nitrogen oxides strongly irritate the respiratory organs, causing inflammatory processes in them; under their influence, methemoglobin is formed, blood pressure decreases, dizziness, vomiting, shortness of breath, loss of consciousness is possible [1, 2]. Atmospheric air pollution ranks first in terms of the degree of chemical danger to humans, which is due to the fact that pollutants from the air have the widest distribution [3]. A noticeable deterioration in the state of atmospheric air in a number of countries occurs due to the most large-tonnage (million tons per year) global atmospheric pollutants: carbon dioxide ($2 \cdot 10^4$), dust (250), carbon (200), sulfur dioxide (150), hydrocarbons (>50), nitrogen oxides NO_x (50) [4]. Pollution of the atmosphere

by harmful substances contributes to research, development and use of more advanced technologies, effective methods and equipment for cleaning waste gases, in particular during the operation of stationary installations [5]. Waste gases, which contain nitrogen oxides, are produced in a number of productions of the chemical industry, in the processes of oil distillation, during the burning of fuel. The sources of emissions of waste gases differ in many parameters: in their content of nitrogen oxides and other impurities, the degree of oxidation of nitrogen (II) oxide, temperature, pressure, etc. [6]. This requires the development of new effective methods of gas purification.

Analysis of recent research and publications. In practice, mainly NO and NO₂ are emitted with the waste gases in their simultaneous presence. Nitrogen (II) oxide NO is poorly soluble in water, salts and organic compounds. Nitrogen (IV) oxide NO₂ is formed as a result of oxidation of nitrogen (II) oxide by oxygen. It easily forms nitrate and nitrite acids with water. Nitrogen (IV) oxide N₂O₄ is formed by the polymerization of nitrogen (IV) oxide NO₂ and is a strong oxidizer. Four classes of methods for cleaning gases from nitrogen oxides are known: oxidative, reducing, sorption, and others. This classification is based on the ability of nitrogen oxides: 1) to oxidize under the action of liquid, solid, and gaseous oxidants; 2) is reduced to nitrogen under the influence of high temperatures and in the presence of liquid, solid and gaseous reducing agents and catalysts; 3) enter into chemical reactions with various groups of compounds, forming various salts and complex compounds that can be regenerated [7, 8, 9].

Oxidative methods of sanitary purification of gases from nitrogen oxides are based on the preliminary oxidation of nitrogen (II) oxide with subsequent absorption of nitrogen (IV) and (III) oxides (NO₂, N₂O₃) by various absorbers.

The main difficulty of absorption processes is related to the low chemical activity and solubility of nitrogen oxide (II). There are several ways to solve this problem: 1) complete oxidation of NO to NO₂ in the gas phase; 2) partial oxidation of NO to NO₂, with the formation of an equimolecular mixture of NO and NO₂; 3) use of selective absorbents; 4) oxidation in the liquid phase or the use of absorption catalysts and conversion of NO into chemically active compounds (NO₂, N₂O₃, N₂O₅) [4]. Industry uses the method of homogeneous oxidation of NO in the gas phase with oxygen. However, as practice shows, at low concentrations of NO, the rate of homogenous oxidation is extremely low. From the kinetic equation

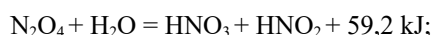
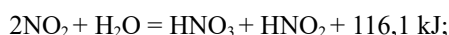
$$\frac{dNO_2}{d\tau} = K P_{NO}^2 \cdot P_{O_2}$$

it can be seen that with a decrease in the NO concentration, for example, from 1,0 to 0,1%, i.e. 10 times, the oxidation reaction rate decreases by 100 times, which leads to the necessity of using bulky and expensive oxidizing volumes. To intensify the process, in some cases oxygen is dosed into the nitrous gas, increasing its content to 8–10% and more. Such a method is not effective due to the extremely small increase in the degree of purification and the low degree of use of dosed oxygen (not more than 0.1–0.5%). The rate of oxidation of nitrogen oxide (II) by gaseous oxygen increases in the presence of catalysts. The most active of them is hopkalite at a temperature of 120°C. Intensification of the processes of oxidation and absorption of nitrogen oxides is also possible by increasing the rate of oxidation of NO in the liquid phase in two variants: oxidation by oxygen and ozone in the liquid phase or simultaneous oxidation and absorption by liquid oxidants. The rate of dissolution of gaseous oxidants (oxygen and ozone) in the liquid phase depends on temperature, pressure, concentration of components, the size of the interfacial surface, turbulence of flows, and so on. The dissolution of oxygen and ozone in the liquid phase is a slow process and limits the process of NO oxidation in the liquid phase. When using liquid oxidizers, the dissolution stage is not limiting. The following oxidants are used for the NO oxidation process: KBrO₃, HNO₃, H₂O₂, KMnO₄, (NH₄)₂Cr₂O₇, Na₂Cr₂O₄, K₂Cr₂O₇ [10].

For the absorption of nitrogen oxides (NO₂, N₂O₃, N₂O₅), water, alkali solutions, selective sorbents, acids and oxidizers are used. When nitrogen oxide (IV) is absorbed by water into the gas phase, a part of nitrogen oxide (II) is released, the rate of oxidation of which at low concentrations is low:



This process is a typical heterogeneous process, including the main stages: 1) diffusion of NO₂ from the gas phase to the liquid phase; 2) chemical interaction with the formation of nitric and nitrous acids; 3) decomposition of nitrous acid with the formation of HNO₃ and NO; 4) diffusion of NO from the liquid phase to the gas phase; 5) oxidation of secondary nitrogen oxide (II) to NO₂, after which the cycle repeats:



The rate of oxidation of NO to NO₂ is the limiting stage of the overall process. Since this reaction takes place in the gas phase, the absorption apparatus must have a sufficiently large free volume, so the absorption process is carried out in multi-stage packed or plate columns. Developed more effective methods of increasing the rate of oxidation of NO, it is possible to achieve a high degree of purification of gases from nitrogen oxides.

The purpose of the study is to select the optimal conditions for the oxidation of nitrogen (II) oxide in gaseous emissions during the operation of stationary installations.

Presentation of the main research material

Carrying out numerous experiments on the absorption of nitrogen oxides by various liquid absorbers, it was noted that the degree of absorption usually exceeded the theoretically possible. Thus, conducting alkaline absorption of nitrous gas containing 1% of nitrogen oxides with a degree of oxidization of 30%, the theoretically possible degree of absorption (assuming that absorption is in the form of N_2O_3) should be 60%. It was established by calculation that in the process of absorption, additional homogeneous oxidation of NO in the gas phase takes place by another 5%. Therefore, the total possible degree of absorption should be 70%. In fact, in experiments in these conditions, the degree of absorption was 80–90% and more.

When analyzing this phenomenon, they came to the conclusion that in the process of absorption, oxidation of nitrogen oxides occurs not only in the gas phase, but also in the liquid phase. Further studies were directed to the intensification of the process of oxidation of nitrogen oxides in the liquid phase. The amount of the liquid phase in the mass transfer process is hundreds and thousands of times less than the gas phase. This gives great advantages, since technological operations with liquid can be carried out in much smaller reaction volumes. Investigation of the nitrogen (II) oxide oxidation process in the liquid phase was carried out on the experimental setup of Fig. 1.

In order to establish a quantitative assessment of the NO oxidation process, the operation of the installation in four modes is provided. Of the four options for the operation of the installation, the first one gives an opportunity to estimate the rate of NO oxidation in the gas and liquid phases, and the second, third and fourth – when NO is oxidized only in the liquid phase. In the studies, the goal was not to achieve a high degree of processing of nitrogen oxides, but only to obtain comparative data on the relative speed of the NO oxidation reaction in the liquid and gas phases. All studies were carried out at atmospheric pressure and a temperature of 20°C.

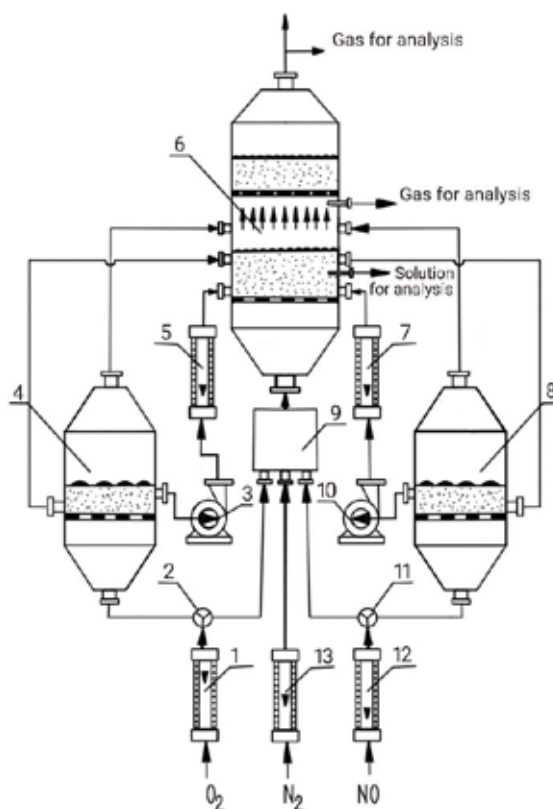


Fig. 1. Scheme of the experimental setup: 1, 5, 7, 12, 13 – rotameters; 2, 11 – three-way faucets; 3, 10 – pumps; 4 – oxygen saturation reactor; 6 – nitrogen oxide absorption reactor; 8 – nitrogen oxide saturation reactor; 9 – mixer

The results of studies of the operation of the installation in all modes are shown in table 1. From the data presented, it can be concluded that with parallel processes, oxidation in the liquid phase proceeds at a slower rate than in the gas phase. The amount of NO oxidized in the liquid phase is approximately 30%. As a result of these studies, it was established that during the absorption of nitrogen oxides from low-concentration and low-oxidized gases in order to intensify the process of oxidation and absorption of nitrogen oxides, it is expedient to dose oxygen into the gas phase, bringing its concentration to 6–7%. A further increase in the concentration of oxygen in nitrous gas is ineffective.

Table 1

**Comparative data on the rate of processing of nitrogen oxides during the oxidation of NO
in the gas and liquid phases**

Mode of operation	Method oxidation	The degree of conversion of nitrogen oxides, %	The relative rate of conversion of nitrogen oxides	The maximum concentration of HNO ₃ , %
I	In gas and liquid phase	63	1	49
II	In the liquid phase when the solution is saturated with oxygen	31	0,456	50
III	In the liquid phase when the solution is saturated with nitrogen oxide	28	0,410	47
IV	In the liquid phase when the solution is saturated with oxygen and nitrogen oxide	26	0,383	50

The principle of oxidation of nitrogen (II) oxide in the liquid phase, studied in the experimental model (Fig. 1), is included in the design of the absorption unit for the production of nitric acid. A distinctive feature of the unit is that an additional column of small diameter, having the same number of plates as the main column, is installed parallel to the main absorption mesh column. Intensification of the process of absorption of nitrogen oxides is possible only by increasing the share of NO oxidized in the liquid phase, which is achieved by saturating the working solution with oxygen in the additional reactor.

Condensate, going to produce nitric acid, first enters the upper plate of the auxiliary column. Here it is saturated with oxygen circulating in a closed cycle. Oxygen-saturated condensate flows through the hydraulic valve to the lower plate of the main column. Here it absorbs nitrogen oxides from the purified gas, after which it again enters the upper plate of the auxiliary column through the drain threshold and the hydraulic valve. On this plate of low concentration nitric acid is again saturated with oxygen and the cycle is repeated again on all plates of the column. This system does not consume a large amount of oxygen, as it circulates in the closed circuit of the additional column and is consumed only for the oxidation of NO. After that, the waste gases practically do not need to be cleaned of nitrogen oxides.

Conclusions

Due to the intensively occurring process of oxidation of nitrogen (II) oxide in the liquid and gas phase, the speed and completeness of the gas absorption process increase.

The maximum concentration of nitric acid is achieved due to the fact that, along with the oxidation of NO in the liquid phase and the saturation of the acid with oxygen, the nitrogen oxides dissolved in it are partially blown off into the small-diameter column. This can be explained by the fact that denitrified and oxygenated nitric acid absorbs nitrogen oxides more fully and more quickly. A similar principle of saturation of working solutions with oxygen can be used in systems operating under atmospheric pressure with acidic or alkaline absorption of nitrogen oxides.

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