

A study of the effect of air temperature on the possibility and rate of formation of nitrogen oxides in boiler flue gases

O A Balandina, S M Puring, D N Vatuzov and E B Filatova

Heat and Gas Supply and Ventilation Department, Samara State Technical University, Academy of Construction and Architecture, Molodogvardeyskaya St., 194, Samara 443001, Russia

E-mail: balandinaolya88@rambler.ru

Abstract. We consider the mechanisms of formation of nitrogen oxides in boiler flue gases. Thermodynamic calculations are used to determine the possibility and rate of formation of nitrogen oxides in the temperature range from 25 to 2000°C. We apply the methods of geometric thermodynamics to demonstrate the changes in the Gibbs free energy of nitrogen oxides formation reactions and determine the conditions of achieving the chemical equilibrium for these reactions. An analysis of concentrations of formed nitrogen oxides and temperatures of the jet flame under different conditions of mixture formation was performed. We produced and analyzed a number of diagrams of distribution of the flame temperatures and nitrogen oxide concentrations in the calculation area for the temperatures of the oxidant of 20, 60, 100, 150 and 200°C. Mathematical simulation of the process of gaseous fuel combustion was performed using FlowVision software package. The analysis of the results showed that the decrease in the temperature of the air supplied as an oxidant results in a considerable drop in the concentration of nitrogen oxides in flue gases without any significant impact on the changes of the flame temperature. The results of the study can be used in addressing the problems of optimization of boiler plants in order to reduce harmful flue gas emissions.

1. Introduction

An increase in energy and heat consumption leads to an increase in harmful emissions polluting the environment [1].

Nitrogen oxides take a prominent place among gaseous toxic components formed during natural gas combustion. These compounds are highly toxic and play an active role in the formation of dangerous atmospheric processes [2]. Nitrogen oxides are considered to be one of the causes of smog and acid rain formation. Increased concentrations of these substances have a harmful impact on human health, in particular, by irritating the mucous membranes of the respiratory tract and the eyes.

The following oxides are formed in the process of combustion as a result of the combination of nitrogen and oxygen, depending on the degree of oxidation: nitric anhydride N_2O_5 , dinitrogen tetroxide N_2O_4 , nitrous anhydride N_2O_3 , nitrous oxide N_2O , nitrogen dioxide NO_2 nitrogen monoxide NO . NO and NO_2 have a practical significance from the environmental point of view.

In order to reduce the impact of combustion products on the atmosphere, it is necessary to optimize the combustion process in such a way as to reduce the concentration of nitrogen oxides in the emissions without reducing the efficiency of the boiler unit. A number of methods aimed at reducing the concentration of oxidant and temperature in the flame zone is applied to reduce the content of nitrogen oxides, as well as methods of recovery of nitrogen oxides in the furnace [3].



The temperature range in the gas path of a boiler unit is in a wide enough range. Maximum local temperatures in furnace chambers of boilers are as high as about 2000 K [4]. At such temperatures, the reaction of nitrogen oxides synthesis from nitrogen and oxygen proceeds at a very high rate. Even after leaving the flue stack, at temperatures under 373 K, the process of formation or transformation of nitrogen oxides continues.

Thus, the study of nitrogen oxide formation reactions at different temperatures, as well as the assessment of the effect of process parameters on the combustion contribute to the identification of modes and methods that result in a reduction in the environmental impact of boiler units and increase their efficiency.

2. Materials and Methods

2.1. Thermodynamic calculation of the Gibbs free energy of nitrogen oxides formation reactions in flue gases of boiler plants

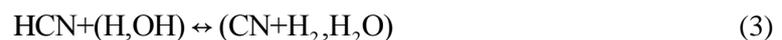
In order to assess the direction of chemical reactions of thermal nitrogen oxides formation in the course of natural gas combustion, we calculate the change of the Gibbs free energy in the temperature range typical for gas paths of boiler units.

The mechanism developed by Yakov Zeldovich determines the yield of nitrogen oxides formed in a reaction between the oxygen atom and the nitrogen molecule [5]. The oxidation of atmospheric nitrogen by free oxygen in the process of combustion is described by the following reaction:



The rate of formation of thermal nitrogen oxides is significantly impacted by the process temperature, as breakdown of O_2 molecules requires overcoming a high energy threshold [6].

Equilibrium concentrations of nitrogen oxides are formed over a period of time equal to 10^{-2} – 10^{-3} seconds. Such rapid formation of nitrogen oxides is explained by binding of nitrogen molecules to radicals CH and C_2 in reactions with low energy threshold, occurring according to the mechanism [7]:



After leaving the flue stack and entering the atmosphere, most of NO is transformed into NO_2 . The oxidation mechanism can be represented by the following reactions [5]:



2.2. Mathematic simulation of nitrogen oxides formation intensity depending on temperature of oxidant fed to the flame

To optimize performance of existing burners, it is necessary to study possible gas combustion modes with varying process parameters which may impact the rate of nitrogen oxides formation. In experimental studies, it is quite difficult to vary parameters in a wide range of adjustment. For this reason, mathematic simulation is utilized to study the combustion modes [8]. The scope of currently known theoretical papers on filtration gas combustion are limited either to analytical review of experiment data, description of physical phenomena and the problem statement or to individual particular calculations based on quite complex models and algorithms or conditions attainable in a laboratory-based experiment [9].

Jet flow simulation is quite relevant especially in using jet gas burners.

A model of gas combustion in a cylindrical burner is proposed and studied below.

FlowVision software package was utilized to study temperature impact of the air supplied to the process as an oxidant on nitrogen oxides formation rate. The mathematical model of the combustion process is based on Navier-Stokes and continuity equations [10]:

$$\left. \begin{aligned} \frac{dv_x}{dt} + v_x \frac{dv_x}{dx} + v_y \frac{dv_x}{dy} + v_z \frac{dv_x}{dz} &= X - \frac{1}{\rho} \frac{dp}{dx} + \nu \left(\frac{d^2v_x}{dx^2} + \frac{d^2v_x}{dy^2} + \frac{d^2v_x}{dz^2} \right), \\ \frac{dv_y}{dt} + v_x \frac{dv_y}{dx} + v_y \frac{dv_y}{dy} + v_z \frac{dv_y}{dz} &= Y - \frac{1}{\rho} \frac{dp}{dy} + \nu \left(\frac{d^2v_y}{dx^2} + \frac{d^2v_y}{dy^2} + \frac{d^2v_y}{dz^2} \right), \\ \frac{dv_z}{dt} + v_x \frac{dv_z}{dx} + v_y \frac{dv_z}{dy} + v_z \frac{dv_z}{dz} &= Z - \frac{1}{\rho} \frac{dp}{dz} + \nu \left(\frac{d^2v_z}{dx^2} + \frac{d^2v_z}{dy^2} + \frac{d^2v_z}{dz^2} \right), \\ \frac{dv_x}{dx} + \frac{dv_y}{dy} + \frac{dv_z}{dz} &= 0, \end{aligned} \right\} \quad (12)$$

where t is time in seconds; x, y, z are the particle coordinates; v_x, v_y, v_z are the particle velocity projections; X, Y, Z are volume force projections; p is pressure in Pa; ν is kinematic viscosity, m^2/s ; ρ is density, kg/m^3 .

Combustion process is represented as a gross reaction:



where W is the reaction rate.

For fuel and oxidant flows, which are not preliminary mixed, W gross reaction, rate is determined by turbulent mixing rate (Magnussen model) [11]:

$$W_{\max} = 23,6 \left(\frac{\mu \varepsilon}{\rho k^2} \right)^{1/4} \rho \frac{\varepsilon}{k} \min \left(f, \frac{o}{j} \right) \quad (14)$$

where f is fuel concentration; o is oxidant concentration; j is the weight-based stoichiometric factor; μ is turbulent viscosity $kg/m \cdot s$; ρ is density, kg/m^3 ; k is pulsation; ε is turbulence scale; W_{\max} is the rate of combustion of a flow of unmixed components.

The calculation area was set as $40 \times 200 \times 8$ mm with gas jet entry point in the center of the leftmost edge. The gas jet was supplied at the rate of $v=0.003374$ $kg/(m^2 \cdot s)$ through the section of 8×8 mm. The air jet was supplied with velocity of $v=0.07445$ $kg/(m^2 \cdot s)$ through two symmetrically located sections 16×8 mm [11].

Diagrams of concentrations NO_x^{therm} and temperatures in the calculation area were made based on the calculations.

3. Results

3.1. Results of calculations of ΔG changes in reactions of formation of nitrogen oxides in flue gases of boilers

Thermodynamic calculation of reactions with nitrogen oxides formation during gas fuel combustions in boiler furnaces shows the possibility and direction of processes in the temperature range from 25 to 2000 °C.

Direction of nitrogen thermal oxides formation for the reaction (1) was assessed with the calculation of Gibbs free energy (ΔG) changes.

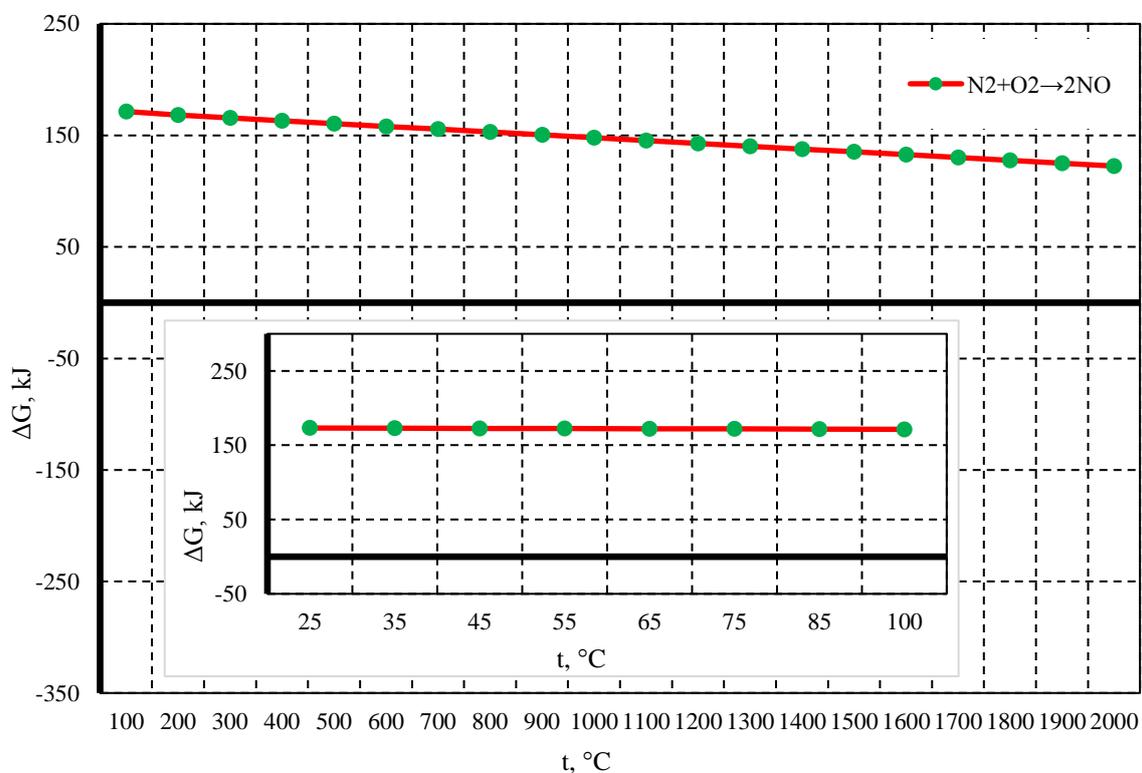


Figure 1. Temperature dependence of ΔG changes in the reaction of thermal nitrogen oxides formation for temperature range of 25÷2000 °C.

For comparative assessment of nitrogen compounds binding with radicals CH and C₂ in low energy barrier reactions, ΔG calculation were done (2÷8) for the following temperature ranges (Figures 2 and 3):

- specific for processes taking place in the furnace chamber and gas duct of the boiler unit (100÷2000 °C);
- specific for processes taking place after the emission of flue gasses into the atmosphere (25÷100 °C).

Results of oxidation reaction direction NO to NO₂ based on the Gibbs energy changes (9÷11) for the temperature range from 25 to 100°C, taking into account temperature decrease in gases exhausted in the atmosphere are shown at Figure 4.

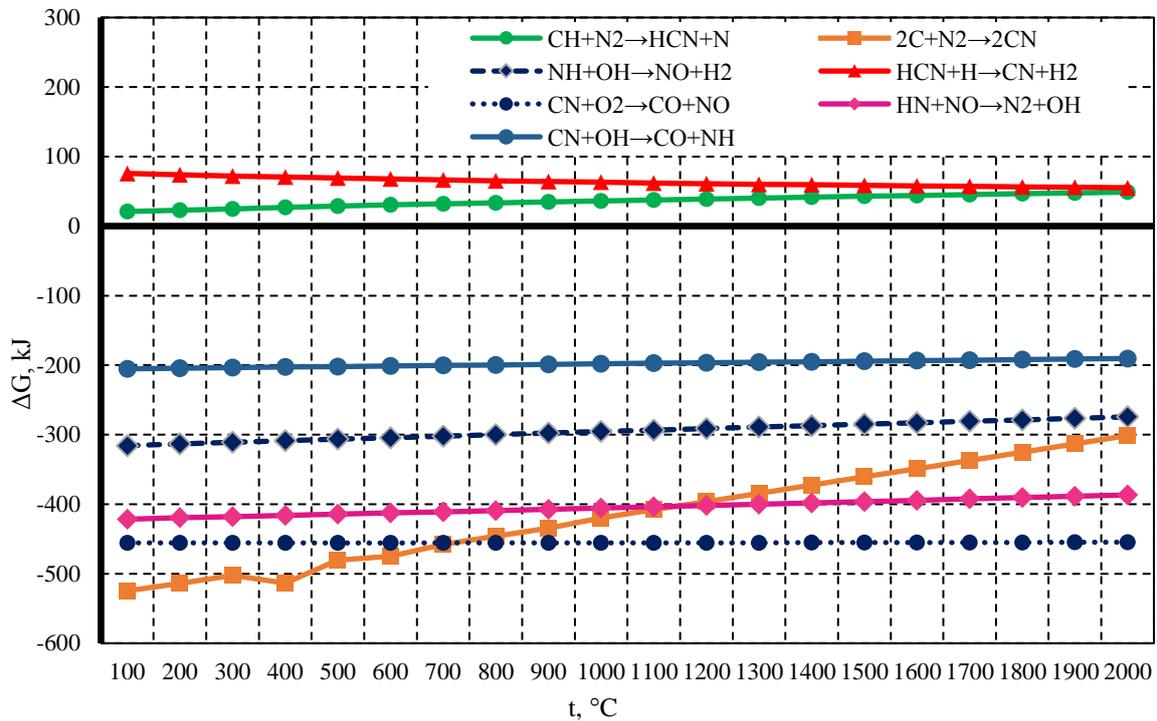


Figure 2. Temperature dependence of ΔG changes in the reactions (2÷8) for the temperature range of 100÷2000 $^{\circ}\text{C}$.

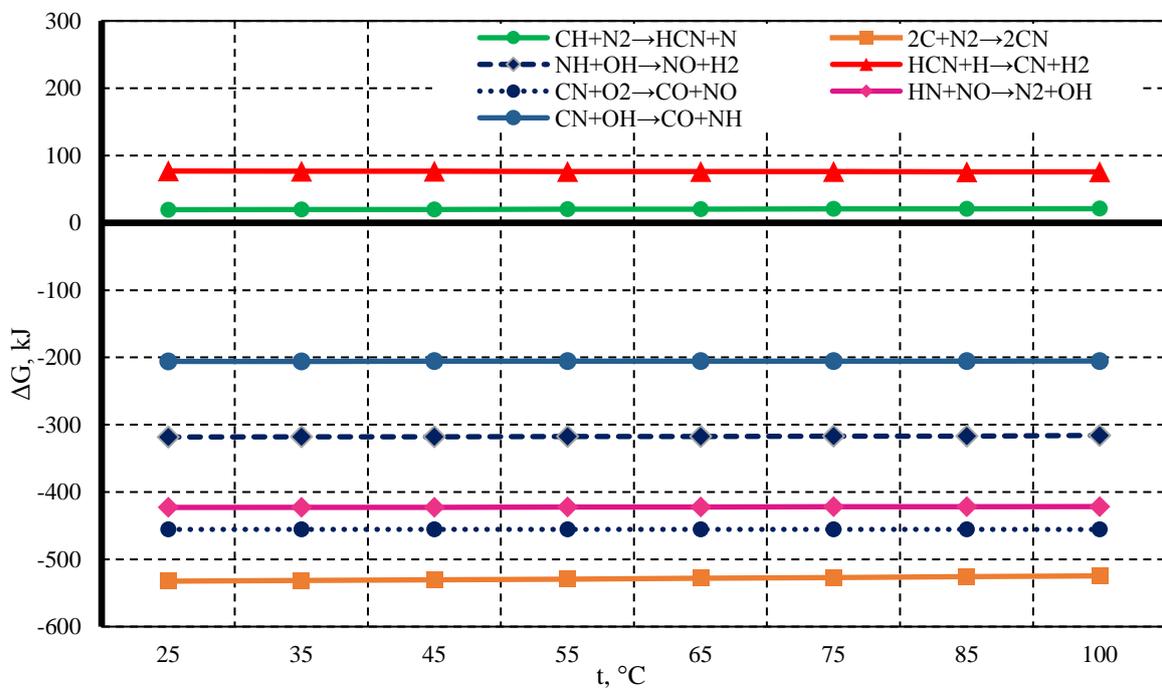


Figure 3. Temperature dependence of the Gibbs free energy changes in Reactions (2÷8) for the temperature range of 25÷100 $^{\circ}\text{C}$.

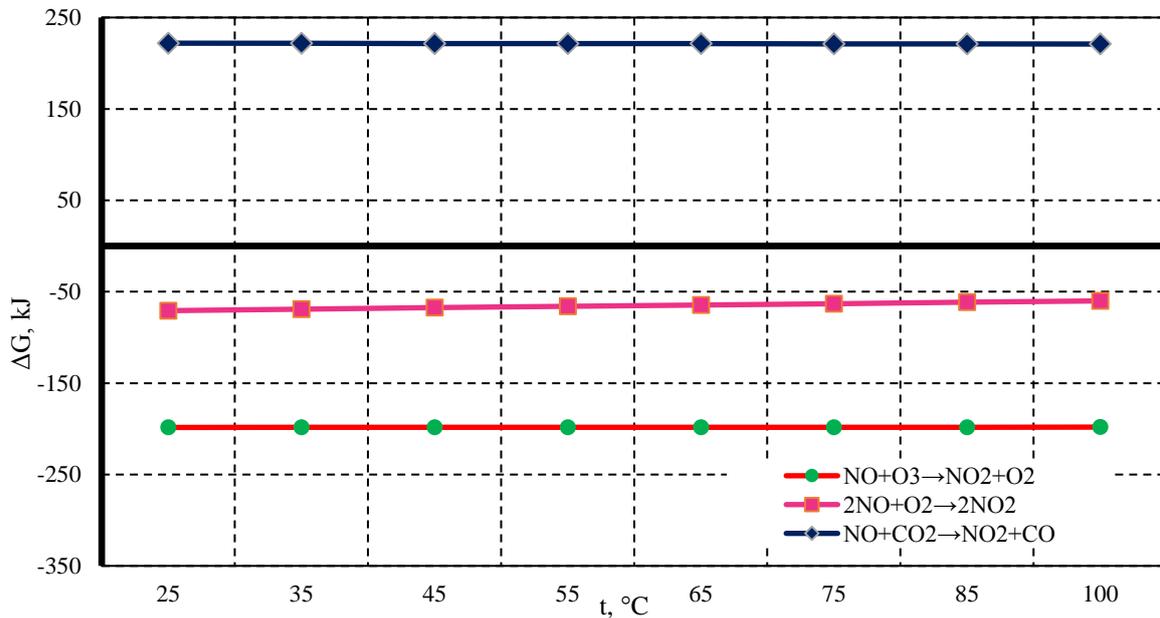


Figure 4. Temperature dependence of the ΔG change in the reactions (9÷11).

3.2. Results of calculation of nitrogen oxides formation rate, depending on the temperature of oxidant supplied to the combustion flame

The simulation included calculations for air temperatures of 20, 60, 100, 150 and 200°C. We obtained distributions of temperatures and concentrations of nitrogen oxide for the five considered options (Figures 5 and 6), depending on the distance from the burner nozzle.

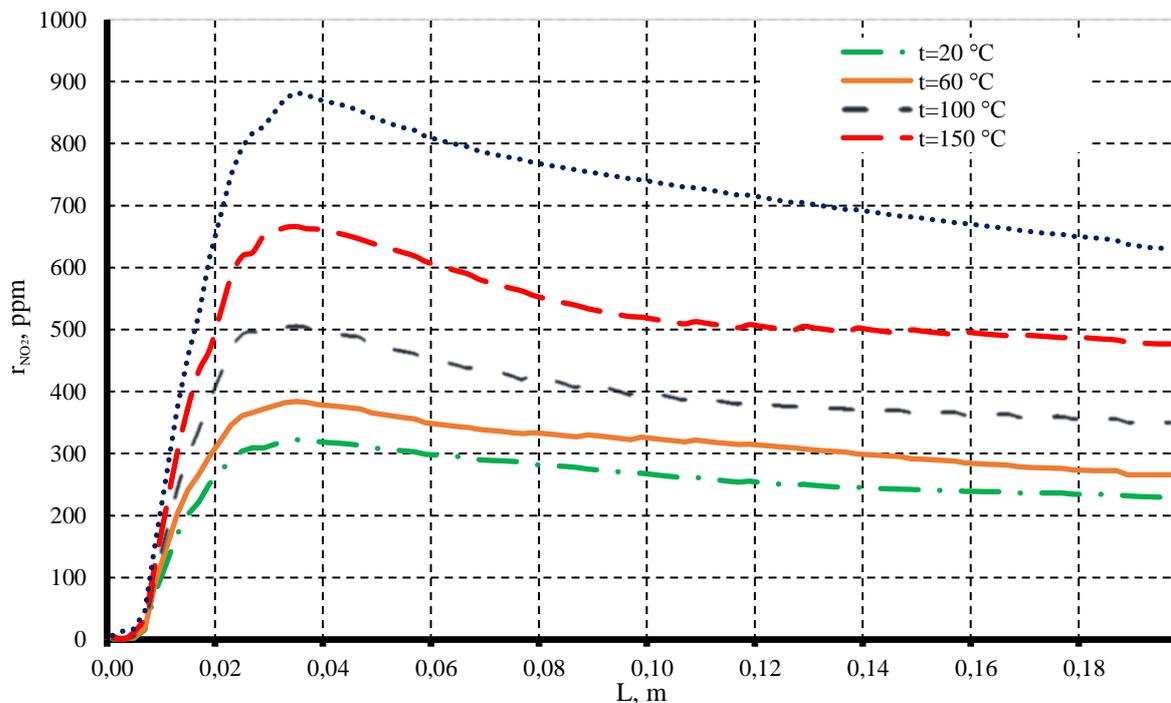


Figure 5. Distribution diagram of nitrogen oxides concentrations along the length at different oxidant temperatures.

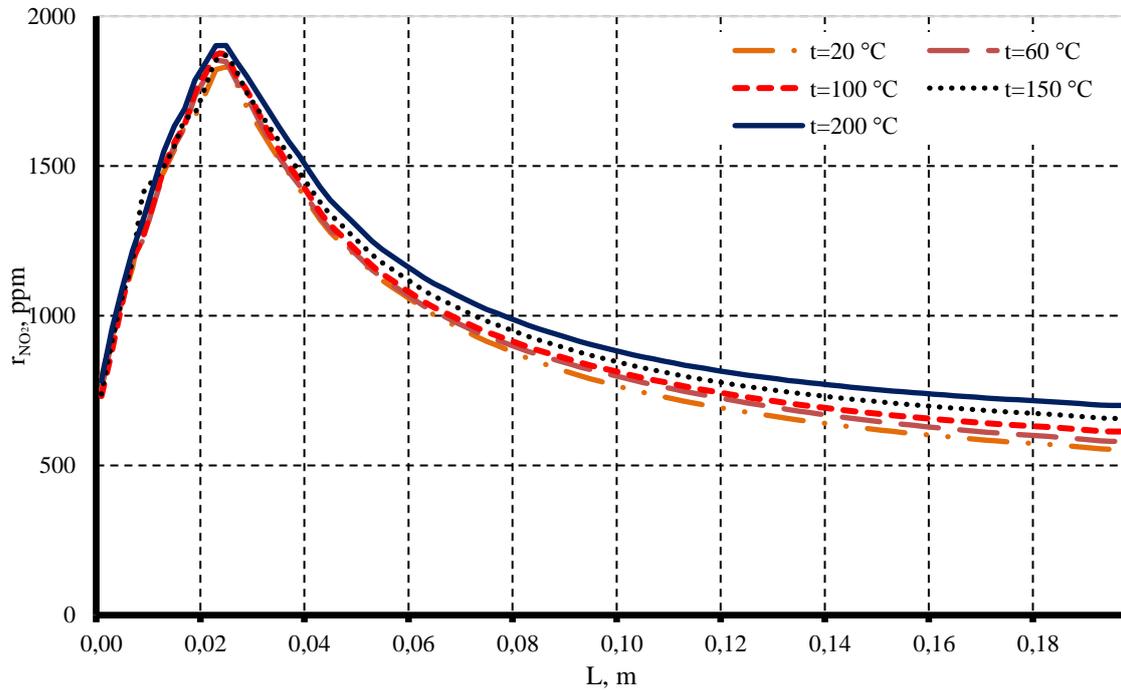


Figure 6. Distribution diagram of flame temperatures along the length in the calculation area at different oxidant temperatures.

The diagram of the dependence of nitrogen oxides concentrations by furnace sections at different oxidant temperatures is shown in Figure 7.

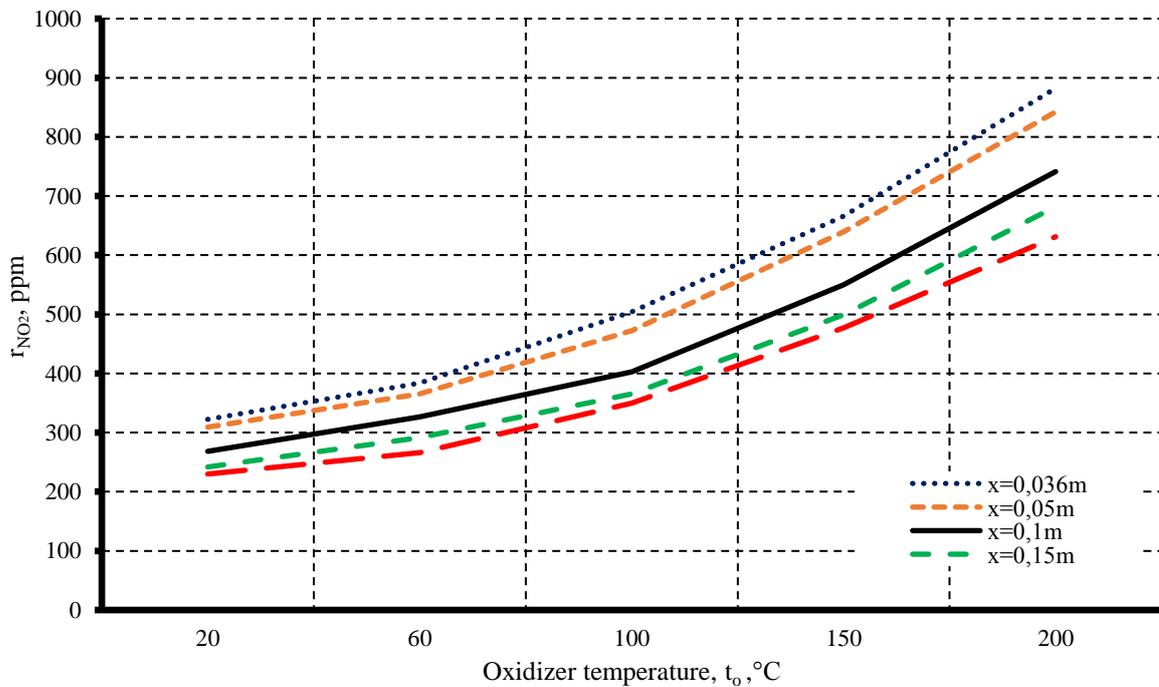


Figure 7. Dependence of nitrogen oxides concentrations by furnace sections at different oxidant temperatures.

4. Discussion

4.1. Study of changes in ΔG of reactions of nitrogen oxides formation in boiler flue gases

Thermodynamic calculations of the reaction (1) show that thermal nitrogen oxides formation process is not accompanied with heat generation, changes of Gibbs free reactions have positive values, therefore, the equilibrium of the considered reaction in the range of temperatures from 25 to 2000 °C will be shifted to the left. Thus, it can be concluded according to the data from Figure 1 that thermal nitrogen oxides will not be formed in the considered temperature range. Considering that thermal NO oxides form mainly in a narrow temperature range $[T_{\max} \div (T_{\max} - 60K)]$ [12], it can be concluded that steady-state concentrations are not achieved during nitrogen oxides formation in the furnaces of boilers and, therefore, concentration of NO in flue gases depends on chemical reactions kinetics [13-15].

According to Figures 2 and 3 it can be concluded that nitrogen molecules and radicals binding reactions CH and C₂ according to the formulas (2÷3) in the considered temperature ranges proceed in the opposite direction, therefore, the probability of cyan molecules formation during these reactions is minimal. Exothermic reactions (4÷8) in the considered temperature range have negative values, which is indicative of a rather significant equilibrium shift to the right.

It follows from figure 4 that reactions (9, 10) are prevailing, as they proceed at all temperatures of the studied range. The equilibrium of the endothermic reaction (11) in the range of considered temperatures is displaced to the left, as evidenced by positive values of variation parameters of the Gibbs free energy. Therefore, this reaction proceeds in the opposite direction.

In addition to "thermic" and "fast" mechanisms of nitrogen oxides formation in the combustion area mentioned above, there is another "fuel" mechanism depending on nitrogen content in fuel and the presence of excess air. However, no nitrogen oxides formation according to the later mechanism does occur during flame combustion of natural gas.

4.2. Calculation of nitrogen oxides formation rate depending on the temperature of oxidant supplied to the flame

As it follows from Figure 5, formation of thermal nitrogen oxides in combustion of natural gas significantly depends on the temperature of air supplied to the burner to produce gas and air mixture. The maximum values of volume concentration of nitrogen oxides are observed at the oxidant temperature of $t = 200$ °C.

Based on Figure 6, it can be concluded that the temperature of oxidant supplied to the combustion area has only a minor effect on temperature distribution in the flame area.

Dependence of nitrogen oxides concentrations (Figure 8) on sections of the furnace space at various temperatures of oxidant can be described by equation

$$r_{\text{NO}_2} = ae^{bt_0} \quad (15)$$

where a , b are coefficients depending on the position of the furnace section and the oxidant temperature ($a=239.25 \div 166.9$; $b=0.2604 \div 0.2564$).

The convergence of the simulation data with the proposed exponential dependencies is characterized by $R^2=0.9933$ determination coefficient.

5. Conclusion

The above thermodynamic calculations of the reactions proceeding with the formation of nitrogen oxides in the course of combustion of gaseous fuels in boiler furnaces demonstrate the possibility and direction of processes in the temperature range of 25 to 2000 °C. According to the diagrams, we can conclude that reactions do not start until the reactant disappear and stop at a particular state of chemical equilibrium. From a practical perspective, it is important to know the equilibrium shift and at what conditions it happens, making it possible for us to find out the maximum achievable yield of end products. To accomplish this, it is necessary to find the parameters responsible for the chemical equilibrium shift in the required direction. Therefore, by applying the methods of geometrical thermodynam-

ics, we demonstrate that nitrogen oxides formation by the combustion of gas fuel results in the equilibrium being almost completely shifted to the right.

Data obtained from the mathematic simulation of nitrogen oxides formation rate depending on the air temperature indicate that the temperature of oxidant flow greatly impacts the distribution of nitrogen oxide concentration in flue gases: a decrease in temperature of air fed as an oxidant results in nitrogen oxides concentration in flue gases decreasing; the maximum concentration decrease is observed at air temperature of 20°C when temperature in the flame zone decreases insignificantly.

This study considers only one of many factors impacting the level of nitrogen oxides formation in flue gases of boiler units, but the method of numerical calculation of natural gas combustion process characteristics makes it possible to study a wide range of changing parameters.

The proposed model can be used to obtain tentative values of temperatures in the combustion area and flue gas nitrogen oxides concentrations. For boiler unit operation optimization, including the development of effective solutions to reduce nitrogen oxides levels, investigation of a variety of parameters is necessary, which implies further studies.

References

- [1] Liang F Y, Ryvak M, Sayeed S and Zhao N 2012 The role of natural gas as a primary fuel in the near future, including comparisons of acquisition, transmission and waste handling costs of as with competitive alternatives *Chemistry Central J.* **6(1)** S4
- [2] Smirnov B Yu 2015 Termodinamicheskiy analiz vosstanovleniya oksidov azota v otkhodyashchikh dymovykh gazakh [Thermodynamic analysis of the reduction of nitrogen oxides in exhaust flue gases] *Akademicheskii zhurnal Zapadnoy Sibiri* **11 1(56)** 122-3 [In Russian]
- [3] Kamalova G A, Tulegenov K K, Rakhmetova K B and Ramazanova K M 2018 Three-dimensional modelling of gas-air mixture combustion process *J. of King Saud University* **10** 1-13
- [4] Habib M A and Elshafei M 2006 Computer simulation of NO_x formation in boilers *MSV 2006* (Las Vegas, Nevada, USA) 94-100
- [5] Michos K, Bikas G and Vlaskos I 2016 A new global algebraic model for NO_x emissions formation in post-flame gases-application to lean premixed combustion systems *SAE 2016 World Congress and Exhibition* [Technical Paper 2016-01-0803]
- [6] Srivastava R K, Hall R E, Khan S, Culligan K and Lani B W 2005 Nitrogen oxides emission control options for coal-fired electric utility boilers *J. of the Air & Waste Management Association* **55** 1367-88
- [7] Chuang, Kai-Hsiang, Kuo-Chuang Chiu and Kuan-Yi Li Composition and apparatus for purifying nitrogen-oxide-containing gases (U.S. Patent Application 10/252 215)
- [8] Satyavada H and Baldi S 2018 Monitoring energy efficiency of condensing boilers via hybrid first-principle modelling and estimation *Energy* **142** 121-9
- [9] Alekseenko S V, Kuznetsov V A, Mal'tsev L I, Dekterev A A and Chernetskii M Y 2019 Analysis of combustion of coal-water fuel in low-power hot-water boiler via numerical modeling and experiments *J. of Engineering Thermophysics* **28 (2)** 177-89
- [10] Arpaia F 2019 *Laminar flame speed prediction for Natural Gas/Hydrogen blends and application to the combustion modeling in IC Engines (Tesi di Laurea Magistrale)* URL <https://webthesis.biblio.polito.it/10725/1/tesi.pdf>
- [11] FlowVision Version 2.5.4. Primery resheniya tipovykh zadach [Examples of solving typical problems] URL <http://flowvision.ru/index.php/public-downloads/category/8-dokumentatsiya-flowvision>
- [12] Castoldi L, Matarrese R, Morandi S, Righini L and Lietti L 2018 New insights on the adsorption, thermal decomposition and reduction of NO_x over Pt-and Ba-based catalysts *Applied Catalysis B: Environmental* **224** 249-63
- [13] Sigal I Y, Smikhula A V, Sigal O I, Marasin O V and Kernazhytska E S 2018 Features of the

influence of recirculation of combustion products on the formation of nitrogen oxides in boilers during burning natural gas *Energy Technologies & Resource Saving* **4** 62-8

[14] Morris W J, Baldrey K E, Senior C and Bisque R 2018 U.S. Patent Application 15/941 522

[15] Guan C 2019 Kinetic study of dry reforming of Methane with Ni over different supports and Pt/Al₂O₃ URL <https://doi.org/10.14279/depositonce-8655>