The control of NO_x concentration in natural gas combustion process

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Introduction

The increase in industrialization and related with it activities of energy production and use has caused great interest of the air cleanliness state. At the present stage of development of technology, fuel chemical energy covers the electricity, heat and mechanical energy demand in the world in 90–95%. Fuel combustion is the main cause of anthropogenic pollution. During these processes are generated and emitted more than 100 different kinds of harmful substances, including about 70% of NO_x and SO_2 emission, about 60% of CO, about 55% of the emission of particulate matter and 98% of CO_2 emission. The least problems poses natural gas combustion. Appreciable risk of this process is the emission of nitrogen oxides. Less favorable to the environment is the liquid fuels combustion, especially when it takes place in the diffusion flames. In addition there is also emitted carbon monoxide, unburned hydrocarbons and particulate matter. The most "dirty" technology, is the coal combustion. In Poland, 97% of primary energy is obtained from its combustion [2, 5, 8, 9, 28].

Oxidation of nitrogen associated with the combustion process leads to the emission of pollutants, which pose a significant threat to the environment. The products of this process are present in the atmosphere mainly in the form of NO, NO_2, N_2O. Their emissions are given as the sum of NO and NO_2 referred to collectively as NO_x. From a hundred fifty years, these emissions are steadily rising and are a major air protection problem. In the mid-twentieth century was clearly ascertained that NO_x involved in the chain reaction of interferes the balance of ozone in the atmosphere that lead to photochemical smog formation. Furthermore NO_2 and N_2O are greenhouse gases. As a consequence of these facts adequate provisions for the prevention and control of pollution commonly known as the IPPC Directive were implemented [4, 6].

Since 2001 in Poland the Environmental Protection Law is held true, which clearly defines the requirements and introduces mandatory emission limits of NO_x for producers [6].

Studies of nitrogen oxides (NO_x) formation from fuel combustion have more than fifty years history. Their main task is to stop the continuous increase of NO_x emissions to the atmosphere. However, it should be noted, that the most difficult part of their reduction is to precisely determine the mechanisms of NO_x formation .

The concentration of NO_x is primarily dependent on [9, 12, 15, 32]: share of the nitrogen in fuel, combustion temperature, the ratio of air to fuel, residence time in the reaction zone.

During combustion of natural gas using conventional gas burners with a capacity of tens megawatts, the participation of NO_x is up to 300 mg/m³. In the case of conventional burners use in heating aggregates, participation of NO_x is in the range of 35–140 mg/m³. However, if the combustion air is preheated, then participation of NO_x in the flue gas can exceed 2000 mg/m³ [11, 20, 22÷26, 30].

The subject of this study has found its source in numerous publications in the field of expanded mechanism of thermal NO, in which the important role of nitrous oxide N_2O was emphasized. Reactions of NO formation via nitrous oxide N_2O are not yet well

understood. Many of suggestions to clarify the reaction are a scientific hypothesis. Measuring greenhouse gas is one of the most important elements of air protection. Only in this way may be obtained the most objective information about the degree of risk in the atmosphere. In addition, the emission results provide direct evaluation level of responsibility of individual plants for air pollution [2, 7, 14, 29].

The first accurate method of NO_x determination have been developed in the forties of the twentieth century. Currently, the detection and measurement of nitrogen oxide in the air and flue gas can be used classic and instrumental methods of chemical analysis [3].

The oldest methods of NO_x measurement are colorimetric methods, which include inter alia: the methods based on the Griess – Ilosvay, Jacobs, Salzman reaction with subsequent modifications and the method of Sawicki, Johnson and Stanley. All these methods are based on chemical treatment of the purified gas by mixing it with various chemical compounds. The received substance absorbs light of a certain length, and the degree of absorption is a measure of nitrogen oxide content. These methods are now rarely used because of the complexity of carrying out a chemical treatment, a long measuring time (coming up to several hours) and the lack of automation [19].

The literature analysis has shown that the most frequently used methods for the determination of NO_x are [3, 19, 27, 31] : coulometric, chemiluminescent, gas chromatography, infrared spectroscopy, gas chromatography coupled with spectroscopic methods.

Depending on the method, nitrogen oxides directly in the gas phase in the form of intact are determined or during the measurement NO_x to other chemical compounds contained in the gas phase or in solution are processed [3, 5, 19, 27, 31].

Among these methods only gas chromatography and spectrophotometric infrared method allow for N_2O analysis in the flue gas. Other methods measure the concentrations of NO, NO_2, or give the measured values in the form of NO_x [3, 31].

Apart from determination of nitrogen oxides by measuring methods, noteworthy are professional computer programs such as CHEMKIN, CHEMCAD, KIVA and others [1, 13, 16, 17, 21]. Thanks to them it is possible to predict the chemical composition of fuels combustion products.

This paper presents the results of experimental and modeling confirming the effect of selected process parameters on the amount of nitrogen oxides formed in the flue gas.

Materials and methods

The aim of research described in this paper was to control the concentration of nitrogen oxides in a laboratory electric- gas furnace KS 520 for various parameters of natural gas combustion process, namely for:
- three temperature ranges of furnace, i.e. 600, 800 and 1100°C
- various excess air ratio λ, i.e.: from 0.9–1.3.

Under the study the laboratory experiments and numerical calculations using the CHEMKIN software were carried out.

Experimental research were carried out on an experimental stand as shown in Figure 1.
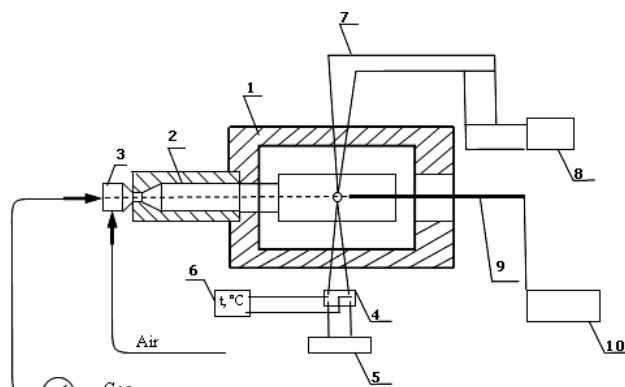
Fig. 1. The scheme of experimental position, where: 1 – furnace, 2 – combustion chamber, 3 – torch, 4 – compensation can, 5 – temperature indicator EMT-302, 6 – regulatory thermocouple PtRh-Pt, 7 – programmable temperature controller, 8 – exhaust gas analyzer probe, 9 – exhaust gas analyzer TESTO 350

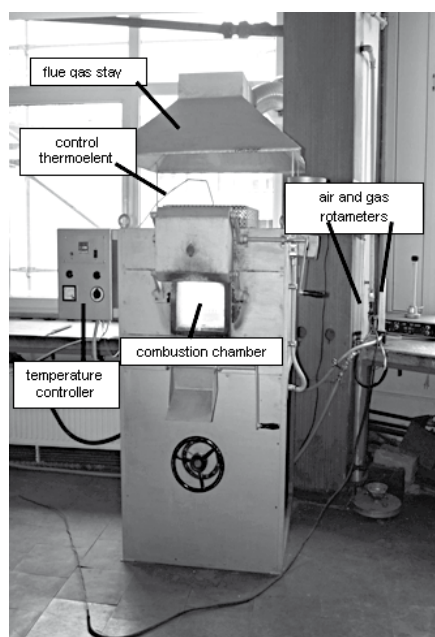General view of the experimental stand is shown in Figure 2

Fig. 2. General view of experimental stand

The main element of the experimental stand was an electric furnace and the combustion chamber with the kinetic gas torch, which in the value of the excess air ratio and thus, the flue gas composition was regulated. The remaining thermal power of the furnace in the form of electricity was supplied, which made it possible to precisely regulate the temperature at any point of the furnace heating chamber. In order to measure the concentration of nitrogen oxides was used gas analyzer TESTO 350. Analyzer probe was placed in the center of the axis of combustion chamber. The research were performed at 1100°C. Desired temperatures were set and maintained using the temperature controller TROL – 9090. The temperature measurements were done with use regulatory thermocouple PtRh-Pt and three supplementary thermocouples NiCr-Ni that were placed at distances of 11, 16 and 40 cm from the torch. The required excess air ratio was adjusted by appropriate valve control system that enables the accurate setting of air and gas jets. Gas and air flows were measured using rotameters. The research were consisted of measuring NO_x concentrations at different values of excess air ratio, which were in the range from 0.90 to 1.30 (measured at 0.05). Determination of excess air ratio below unity was not possible using the analyzer, but it was achieved on the basis of settings of gas and air streams.

Numerical calculations were performed using program CHEMKIN-PRO. In the calculations was used an extended mechanism of methane combustion based on Miller-Bowman mechanism covering 132

chemical reactions and 36 compounds and chemical elements [18]. In order to formulate the boundary conditions in modeling procedure were determined the necessary data, such as: air stream, gas stream, temperature, flue gas velocity.

The data necessary for the modeling studies were summarized in Table 1. Media streams such as air and gas streams were converted to mass streams expressed in kg/s using the density of the reactants. For the calculations the following density were used (at temp.20°C):

- air – 1.29 kg/m³
- nitrogen – 1.25 kg/m³
- methane 0.71 kg/m³
- ethane – 1.32 kg/m³
- dioxide carbon 1.96 kg/m³
- Gas density was 0.724 kg/m³

Table 1

Selected parameters of the media flow

Excess air ratio, λ	Air stream [m³/s] x10³	Gas stream [m³/s] x10³	Gas mass stream [kg/s] x10³	Air mass stream [kg/s] x10³	Reagents mass stream air+ gas [kg/s] x10³
0.90	1.39	0.1658	0.120	1.7915	1.9115
0.95	1.39	0.1569	0.113	1.7915	1.905
1.00	1.39	0.1491	0.108	1.7915	1.8994
1.05	1.39	0.1422	0.103	1.7915	1.8944
1.10	1.39	0.1355	0.098	1.7915	1.8896
1.15	1.39	0.1297	0.094	1.7915	1.8854
1.20	1.39	0.1244	0.090	1.7915	1.8815
1.25	1.39	0.1194	0.085	1.7915	1.8779
1.30	1.39	0.1147	0.083	1.7915	1.8745

The fuel and oxidant (air) were fed into the combustion chamber in the form of fuel – air mixture. The composition of fuel – air mixture is expressed in the molar fractions and are shown in Table 2.

Table 2

Composition of the fuel-air mixture expressed in mass fraction

λ	CH_4	C_2H_6	CO_2	O_2	N_2
0.90	0.1033	0.0006408	0.0001068	0.18764	0.70814
0.95	0.0983	0.0006102	0.0001017	0.18868	0.71196
1.00	0.0937	0.0005814	0.0000969	0.18973	0.71579
1.05	0.0897	0.0005568	0.0000928	0.19056	0.71885
1.10	0.0891	0.0005340	0.0000890	0.19139	0.72191
1.15	0.0828	0.0005136	0.0000856	0.19202	0.72420
1.20	0.0795	0.0004932	0.0000822	0.19286	0.72727
1.25	0.0765	0.0004746	0.0000791	0.19349	0.72957
1.30	0.0739	0.0004584	0.0000764	0.19391	0.73108

For the calculations was assumed a constant temperature of provided media equal to 20°C. Combustion temperature was determined on the basis of the torch temperature measured at 1100°C.

The results of experimental and modeling research

The results of experimental measurements of the concentration of nitrogen oxides at the outlet of the chamber, depending on the excess air ratio at the three temperatures of the furnace, namely 600, 800 and

1100°C are shown in Figure 3. Whereas, in Figures 4÷6 were shown a comparison of experimental and model research results of excess air ratio influence on the nitrogen oxides concentration.
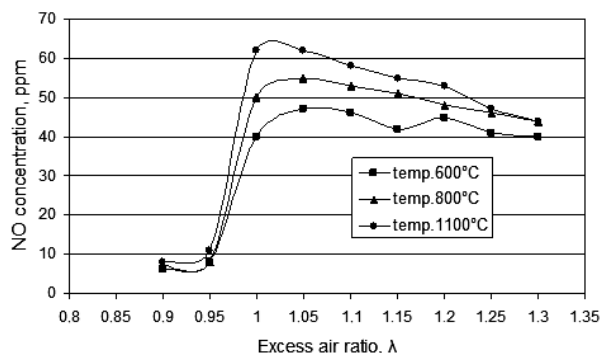

Fig. 3. Dependence NO concentration of the excess air factor

The curves presented in Figure 3 show that temperature in the combustion chamber as well as the excess air ratio have significant effect on the formation of nitrogen oxides.

At the excess air ratio less than one, i.e. $\lambda=0.9$ and $\lambda=0.95$ the concentration of NO_x does not exceed 10 ppm. However, at $\lambda=1.0$ a sharp increase in the NO_x concentration has been observed, i.e. to 40 ppm at 1100°C and 62 ppm at 600°C. Combustion at higher excess air ratio ($\lambda=1.05$) results in a slight increase in the concentration of nitrogen oxides in the flue gas. From the standpoint of nitrogen oxides reduction is preferred to carry out combustion with excess air ratio of less than unity. Unfortunately, the side effect of such process is CO and H_2 occurring in the flue gas.

For a more detailed analysis of the process of nitrogen oxides formation, and thus a better control the numerical calculations were performed. The simulation results were compared with the experimental results (Figs. 4÷6).
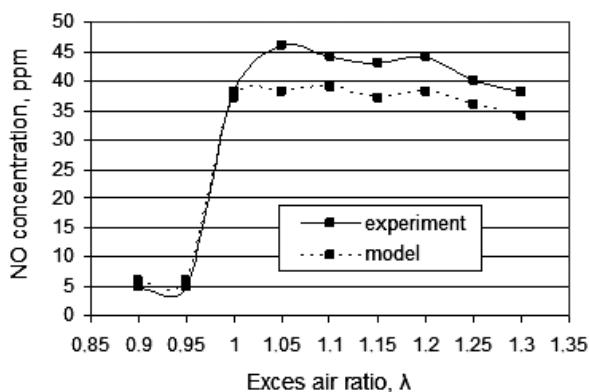

Fig. 4. The comparison of experimental and model results of changing NO concentration depending on the excess air factor at 600°C
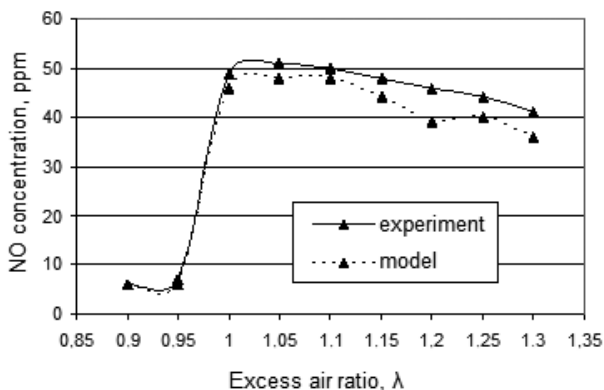

Fig. 5. The comparison of experimental and model results of changing NO concentration depending on the excess air factor at 800°C
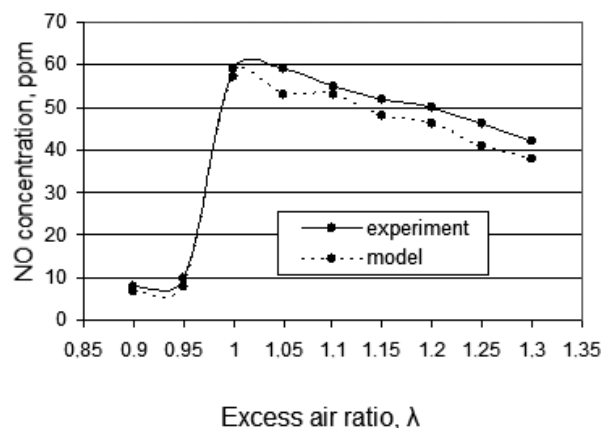

Fig. 6. The comparison of experimental and model results of changing NO concentration depending on the excess air factor at 1100°C

The comparative analysis of model and experimental studies has demonstrated a broad convergence of results. However, it can be noted that the obtained numerical value of nitrogen oxides concentration for all analyzed cases are slightly lower than in the experiment. This has to do with a better mixing of reactants in the combustion chamber as a result of applied the perfect stirring reactor to calculations.

Research has shown that both the temperature and the excess air ratio have a significant effect on the nitrogen oxides formation. A particularly important role in the reduction of NO_x from combustion plays less excess air ($\lambda<1$), which leads to the reduction of nitrogen oxides to a level of a few ppm. At λ in the range of 0.95 to 1.00 can be observed a characteristic peak. At this area the concentration of NO_x increases from a few to several tens of ppm. The maximum concentration of nitrogen oxides (of about 60 ppm at a temperature of 1100°C) occurs at excess air ratio equal to 1.05. Further increase of excess air ratio ($\lambda>1.05$) results in a gradual decrease in the NO_x in the flue gas. Leading combustion process with less excess air the concentration of nitrogen oxides in flue gases is significantly reduced. A side effect of combustion with underflow air was a carbon monoxide CO (0.78%) and hydrogen H_2 (0.38%) formation. Validation of model and experimental results showed high compliance and proved correctness of numerical calculations. Nature of the curves obtained from model research was similar to curves obtained during the course of the experiment. Higher values of NO_x concentrations were during experimental studies, while a little lower for the calculations. That was an effect of perfect stirring of reagents in the burner .

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