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THE ANALYSIS OF NITROGEN OXIDES FORMATION DURING OXYGEN - ENRICHED COMBUSTION OF NATURAL GAS

This paper presents the study of oxygen-enriched combustion of natural gas and its impact on nitrogen oxides emission. The research were performed on two experimental stands, i.e. combustion chambers with an industrial swirl burner of maximum power equal to 90 kW and 10 kW. The investigation includes the influenced of oxygen enhanced within the range between 21% and 30%. Furthermore, the role of temperature during the oxygen enrichment was analysed. The results of the research showed that with the rise in oxygen concentration in the air the concentration of nitrogen oxides also increases what is directly related to the rise in flame temperature as well as the addition of oxygen.

Keywords: oxygen enhanced combustion, nitrogen oxides emission

1. Introduction

Combustion of fossil fuels plays a major role in production of electricity and heat as well as in transport and industrial processes. However, the process is accompanied with a formation of a number of unwanted products, as greenhouse gasses and other air pollutants such as nitrogen oxides, sulphur oxides or particular matters [1]. Concerning the iron and the steel industries, in which many of combustion processes are performed at high temperatures, above 1400°C particularly important group of pollutants are nitrogen oxides. Above that temperature the formation of thermal NO_x is more pronounced. Although emission of nitrogen oxides occurs as a result of both natural phenomena and human activity, the latter one is more harmful due to its higher local concentrations. A whole series of photochemical reactions, in which NO_x are involved, causes a number of adverse environmental effects, such as acid rain, photochemical smog and depletion of the ozone layer, leading to so called ‘ozone hole’. In the processes of fuel combustion two types of NO_x are primarily produced: nitric oxide (NO) and nitrogen dioxide (NO₂). Approximately, 90–95% of the nitrogen oxides generated with the flue gas are in the form of nitric oxide (NO), whereas the remaining amount about 5–10% is represented by NO₂. Thus, air pollution experts refer to NO and NO₂ collectively as NO_x. Other nitrogen oxides, i.e. nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃) and dinitrogen pentoxide (N₂O₅) exist in very small concentrations in the flue gas [2].

Recently, the issue of oxygen-enriched combustion is one of the most intensively developing areas of research in the field of emission reduction and it has become of

interest of many research centers in the country and abroad [3÷9]. Initially, the essence of oxygen enriched combustion was to reduce carbon dioxide emission (Carbon Capture and Storage - CCS) [10÷15]. There are also many other advantages of using oxygen-enriched combustion, among which the most important are: increasing the efficiency of energy production (with the increase in oxygen in the oxidizer the temperature rises) and a reduction of the amount of flue gas and thereby reduction of gaseous pollutants emission such as SO₂ or NO_x [4]. The processes of nitrogen oxides formation during oxygen-enriched combustion are not yet well understood, what leaves wide scope for researchers to undertake analysis related to this topic.

Formation of nitrogen oxides is a very complex issue. The quantity of emitted NO_x strongly depends on temperature, the content of molecular nitrogen in the fuel as well as on the type of oxidant applied into the combustion process. In the oxygen-enriched combustion the total quantity of nitrogen in the combustion chamber is considerably lower in comparison with a conventional combustion in the air and leads to a reduction of NO_x emitted into the atmosphere [16]. The reduction of nitrogen oxides emission in oxygen-enriched combustion means that their amount in relation to the chemical energy of fuel (NO_x, expressed in mg/MJ) is smaller. In turn, shares of NO_x (in ppm) are typically higher [17]. Although, the NO_x concentration expressed in ppm grows up the trend of total NO_x emission decreases compared to the amount of chemical energy of fuel. According to [18] the efficiency of NO_x reduction during the combustion in the oxygen-enriched atmosphere is within the range between 25% and 50% in comparison with the combustion in the air.

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2. Experimental research

The aim of the research was the analysis of the impact of oxygen-enriched combustion within the range between 21% and 30% on the concentration of nitrogen oxides. Experimental studies were carried out on two laboratory stands, namely a cylindrical chambers, being a simplified models of the pusher type reheating furnace. The basic element of the first laboratory stand (Figs. 1, 2) is a cylindrical combustion chamber with an internal diameter of 0.12 m and total length of 3 m. The chamber is divided into three parts. The first one is made of quartz and next two are made of ceramic. In the initial segment of chamber the industrial swirl burner fueled with natural gas of maximum power equal to 10 kW is positioned. In order to achieve a steady state conditions the combustion chamber was heated up to about 1300°C for about 5 hours. At entire length of the chamber fifteen measuring points allowing to measure the temperature are placed. In the case of research presented in this article the temperature was measured at seven points, i.e. in 2, 4, 6, 8, 11, 13, 15. Location of measuring points is presented in Table 1. The air was supplied into the burner with the use of compressor. The oxygen taken from the cylinder was injected directly into the combustion chamber directly through the burner.

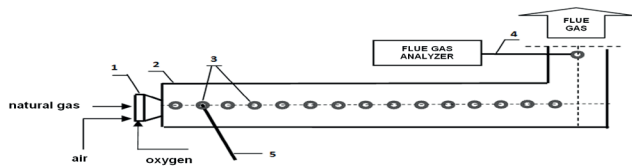


Fig. 1. Scheme of the first experimental stand: 1– burner, 2– combustion chamber, 3– measuring points, 4– gas analyzer probe, 5– thermocouple PtRh10-Pt

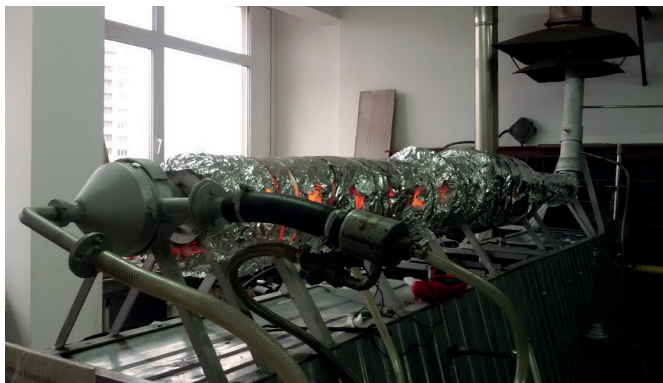


Figure 2. View of the first experimental stand

TABLE 1

Location of the measuring points

Number of measuring point	Distance from the burner outflow, m
1	0.12
2	0.29
3	0.47
4	0.64
5	0.80
6	0.97
7	1.22

8	1.42
9	1.62
10	1.91
11	2.11
12	2.31
13	2.51
14	2.71
15	2.91

The second experimental stand (Figs. 3,4) consists of the cylindrical ceramic combustion chamber with 90 kW gas burner. The temperature was measured at four points, i.e. in 2, 4, 7 and 10 (Table 2). The internal diameter of the chamber was equal to 0.34 m and total length was 3.12 m. The combustion chamber was heated up to about 1300°C for about 12 hours. Temperature in both cases was measured with the use of PtRh10-Pt thermocouple. It was assumed that the temperature measured at the second measuring point was the flame temperature, as the flame kernel was located at that distance from the burner. In turn, flue gas composition was measured at the outflow of the chamber by the automatic analyzer VARIO MRU. The primary air was supplied to the burner with the use of an electric fan and the oxygen was injected from the cylinder. The secondary air was preheated up to 230°C. Media flow rates were measured with the use of the flow meters. Chemical composition of natural gas was as follows: CH₄ = 96.7%; C₂H₆ = 0.7%; CO₂ = 0.1%; N₂ = 2.5%.

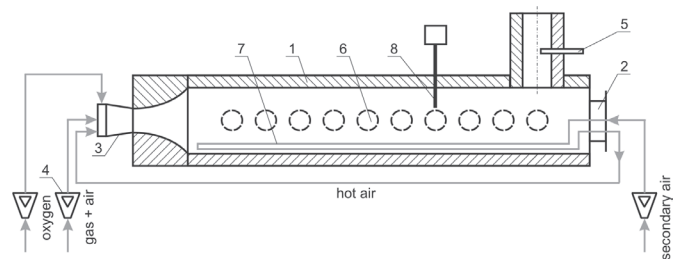


Fig. 3. Scheme of the second experimental stand: 1- chamber, 2 - observation points, 3- burner, 4 - quantity meters, 5- flue gas analyzer, 6- measuring points, 7- secondary air heating pipe, 8 – thermocouple PtRh10-Pt



Fig. 4. View of the second experimental stand

TABLE 2
Location of the measuring points

Number of measuring point	Distance from the burner outflow, m
1	0.11
2	0.37
3	0.64
4	1.17
5	1.45
6	1.72
7	1.97
8	2.25
9	2.51
10	2.78

3. Results and discussion

The research included measurements of NO_x concentration and the temperatures at the outflow of combustion chamber as well as at selected measuring points depending on different values of oxygen content in the oxidizer within the range between 21 and 30%. The study was performed for the excess air ratio $\lambda=1.15$. Table 3 and Table 4 present the values of media streams, i.e. gas (\dot{V}_{gas}), air (\dot{V}_{air}), preheated air ($\dot{V}_{hot-air}$) and oxygen (\dot{V}_{oxygen}) as well as the percentage content of oxygen in the oxidizer. The gas flow rates in both cases were constant while the air and oxygen fluxes were changed.

TABLE 3
The fluxes of provided media of the first combustion chamber

\dot{V}_{gas}	\dot{V}_{air}	\dot{V}_{oxygen}	oxygen content
m^3/h	m^3/h	m^3/h	%
1.62	17.37	0	21.0
1.62	15.68	0.2	22.0
1.62	14.84	0.3	22.6
1.62	14.01	0.4	23.2
1.62	13.18	0.5	23.9
1.62	12.36	0.6	24.7
1.62	11.56	0.7	25.5
1.62	10.76	0.8	26.5
1.62	9.99	0.9	27.5
1.62	9.23	1.0	28.7
1.62	8.49	1.1	30.0

TABLE 4
The fluxes of provided media of the second combustion chamber

\dot{V}_{gas}	\dot{V}_{air}	$\dot{V}_{hot-air}$	\dot{V}_{oxygen}	oxygen content
m^3/h	m^3/h	m^3/h	m^3/h	%
3.38	19.25	17	0	21
3.38	17.11	17	0.45	22
3.38	15.20	17	0.85	23
3.38	13.30	17	1.25	24
3.38	11.87	17	1.55	25

3.38	10.44	17	1.85	26
3.38	9.01	17	2.15	27
3.38	7.82	17	2.40	28
3.38	6.63	17	2.65	29
3.38	5.44	17	2.90	30

The impact of oxygen enrichment on nitrogen oxides concentration (from 21 to 30%) for two analysed experimental stands is presented in Fig. 5. The nitrogen oxides emission increases as the oxygen concentration is enhanced. The addition of oxygen to the air in both cases caused about tenfold increase in the concentration of nitrogen oxides in the flue gas, namely from 167 to 1841 ppm in the case of first combustion chamber and from 121 to 1284 ppm in the case of second combustion chamber. It can be seen in both cases that for 21÷24% of oxygen content nitrogen oxides concentration increases quite slowly, whereas from 24÷30% the rise is more pronounced.

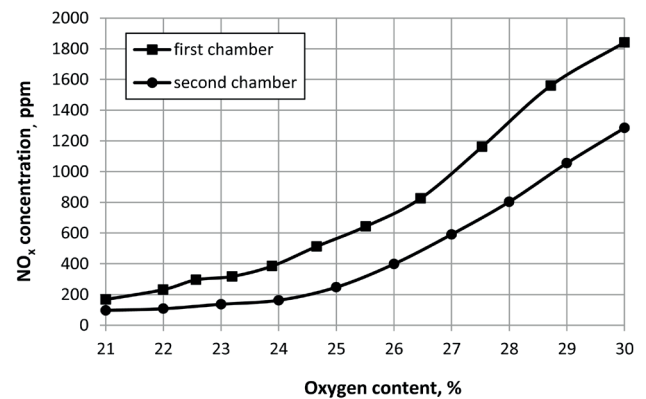


Fig. 5. The influence of oxygen addition on NO_x concentration

In order to explain the discrepancies between the NO_x profiles given in Fig. 5, more detailed analysis is required. Taking into consideration fact, that higher oxygen content in the oxidant causes an increase in flame temperature (see Fig. 6) the rise in NO_x concentration can be related to the thermal mechanism of the nitrogen oxides formation, which primarily occurs at temperatures above around 1400°C [4]. As can be seen from Fig. 6 the almost constant temperature difference inside combustion chambers occurs within entire considered oxygen content. Nevertheless, both NO_x profiles presented in Fig. 5 diverge. Moreover, in the case of first chamber the temperature of 1400°C (activation of thermal mechanism) is reached under 23% of oxygen content and no impact on remaining NO_x formation can be found. On the other hand the influence of temperature on NO_x formation by comparing both chambers (in particular close to the maximum considered oxygen content) is noticeable. Summarising, it can be concluded that the oxygen enhanced has a material impact, even greater than temperature, on NO_x emission within considered ranges of both parameters. More clear correlation between NO_x concentration and the temperature was shown in Fig. 7.

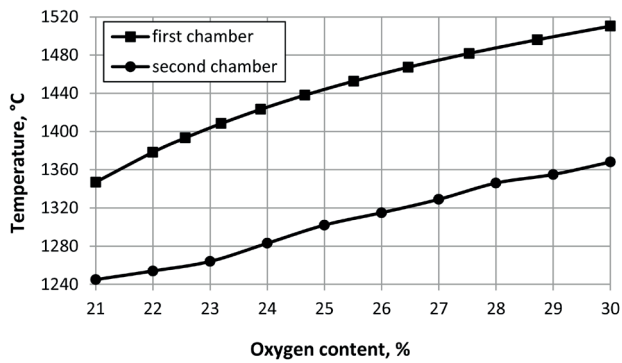


Fig. 6. Flame temperature as a function of oxygen content in oxidant

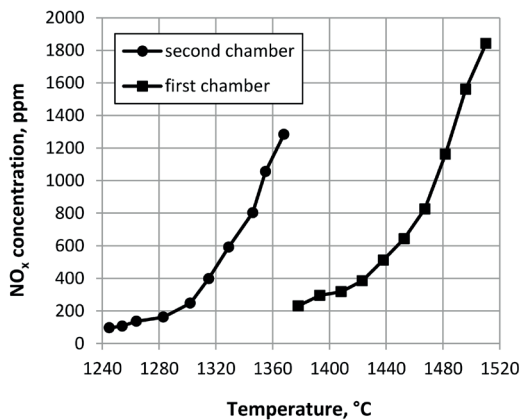
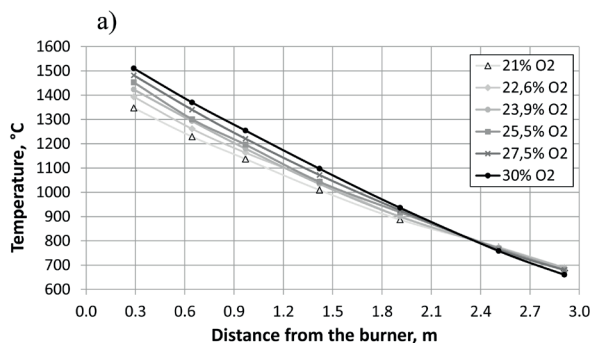


Fig. 7. Nitrogen oxides concentration as a function of flame temperature

Further analysis concerns the temperature distribution along the combustion chamber. Fig. 8 shows temperature profiles for selected oxygen content in the oxidant as a function of the chamber length for the first (a) and the second (b) experimental stand. In both cases the temperature drops with the increasing distance from the burner. Furthermore, it can be seen that this decrease is almost linear. In the first case the flame temperature decreases from



1347°C to 689°C, i.e. by about 658°C when the oxygen content is equal to 21% and from 1510°C to 660°C, i.e. by 850°C when it is equal to 30%. An interesting phenomenon is observed at the outlet of the combustion chamber, where temperature decreases from 670°C to 604°C as the oxygen content is increased (Fig. 9). This fact may be explained by changing the structure and shortening of flame as well as reducing flue gas volume due to addition of the oxygen to the oxidizer. In the second case the flame temperature drop by about 520°C when the oxygen in the oxidizer was 21% and by about 600°C when it was 30%. All measured temperatures at the outlet of the chamber were nearly constant.

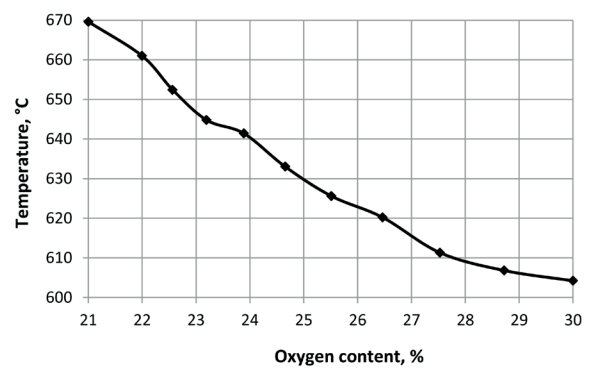


Fig. 9. Temperature at the outlet of the first combustion chamber as a function of oxygen content in oxidant of the first experimental stand

In turn, Fig. 10 presents the NO_x concentration measured at several points at the length of combustion chamber for the first (a) and the second (b) experimental stand. In all cases, both the first and the second combustion chambers NO_x concentration do not change with changing the distance from the burner. It means that the formation of NO_x takes place at the very beginning of combustion process.

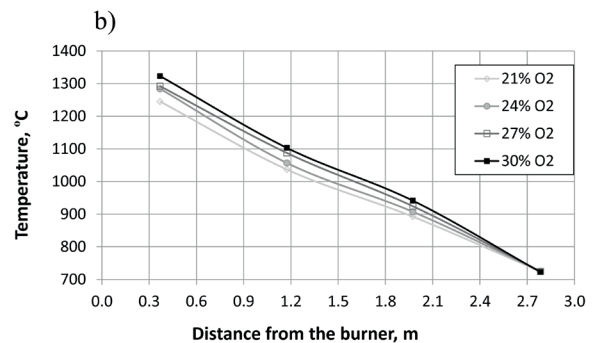


Fig. 8. Temperature profile at the length of combustion chamber depending on oxygen content in the oxidizer; a) the first experimental stand, b) the second experimental stand

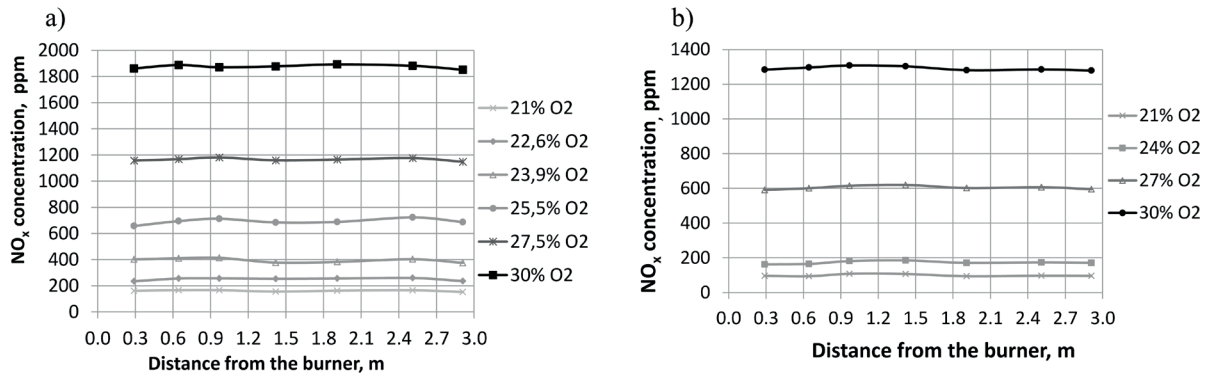


Fig. 10. Nitrogen oxides concentration at the length of combustion chamber depending on oxygen content in the oxidizer, a) the first experimental stand, b) the second experimental stand

4. Conclusions

The oxygen-enriched combustion process can be applied in industrial processes, which require to maintain very high temperatures, for example in the production of steel. Oxygen enrichment combustion causes an increase in the adiabatic flame temperature that also leads to increase in NO_x concentration. Particularly important parameter affecting the formation of nitrogen oxides in the exhaust gas is the temperature. When analysing the effect of the addition of oxygen to the oxidant on the formation of NO_x a special attention should be paid to the impact of the flame temperature. One of ways of nitrogen oxides formation is the thermal mechanism, thus the increase in flame temperature above about 1400°C causes the generation of thermal nitrogen oxides. With increasing concentration of oxygen in the oxidant the temperature also increases what in turn causes a rise in the rate of oxidation of the nitrogen contained in the air and leads to increase in NO_x emissions.

However, the research results presented in this article show that it is difficult to specify which parameter, whether the temperature or an increase in the oxygen content in oxidizer plays a greater role in the process of NO_x formation. In the case of the second combustion chamber, when the flame temperature was below 1400°C , i.e. below the temperature of thermal NO_x formation it can be stated that the increase in nitrogen oxides concentration is caused by the higher oxygen content in oxidizer. That means that the increase in the concentration of nitrogen oxides may be caused by the increased oxygen content in the reactive system, which makes nitrogen included in the air more connecting with oxygen in the high temperatures zone. The injection of an additional amount of oxygen changes the geometry structure of the flame and the high-temperature flame kernel moves back toward the burner. However, it should be remarked that in the case of oxygen-enriched combustion the temperature influence is ambiguous and not fully investigated.

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