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THE REDUCTION OF THE EMISSION OF NO_X IN THE HEAT-TREATING FURNACES

1. INTRODUCTION

The global recession and the economic downturn in 2008 have led to a drop in energy use. The evident decrease of energy consumption up to 2% was observed in the end of 2009. Despite of last energy crisis the fossil fuels are still dominant source of world primary energy. The fossil fuels are going to be ¾ of total energy consumption in next twenty years [1]. This requirement provides increasing of energy production from coal, natural gas and crude oil and the deployment of renewable energy technologies. A significant role between other fuels can get an unconventional gas known as a liquefied natural gas. That situation leads to take an interest in natural gas combustion technologies, especially low-emission combustion. The natural gas is generally used in many branches of industry e.g. in high-temperature combustion processes used in the heat furnaces for heat-treating processes. In spite of many advantages of natural gas, it is also a source of nitrogen oxides generated during combustion. Nitrogen oxides (NO_x) are one of the most important substances resulting from the combustion of fuels. Typical combustion gases contain two kinds of oxides: NO and NO_2. Other kinds of nitrogen oxides are N_2O, N_2O_3 and N_2O_5, but they do not play any essential role. In typical combustion gases from boiler, the volumetric share of NO amounts to about 95% or even more, the rest being NO_2 [2]. NO_2 is a greenhouses gas and one of the California type smog. In the presence of stream water and in the case of atmospheric discharges NO_2 forms nitric acid. NO is not to be so toxic as NO_2. Further more NO is the main source of NO_2, because having been emitted into the atmosphere. The nitrogen oxides are the most harmful substances for environmental, that is why researches study how to reduce NO_x emission. This requires the knowledge of the mechanisms of the formation and reduction of NO_x emissions basing on the kinetics of chemical reactions.

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There are four different mechanisms of the formation of NO: the thermal, prompt, fuel mechanisms and by means of N_2O. The thermal mechanism of NO was described by Zeldowicz [3, 4]. These are the reactions of oxidizing the nitrogen taken from the air at temperature exceeding 1400 °C. The prompt mechanism of Fenimore concerns the combustion of rich mixture of hydrocarbons and air. Prompt NO are formed rapidly in the course of the combustion, immediately before the front or just in the front of the flame. In industry the role of prompt NO is insignificant. The fuel NO is formed from fuel nitrogen in the front of the flame and its amount increases with the growing concentration of oxygen. The concentration of fuel NO in the global emission of nitrogen oxides grows with the decrease of the heat release of the combustion chamber [5].

The main source of NO in the natural gas combustion (with small amount of nitrogen fuel) is the thermal NO mechanism.

2. THE REDUCTION METHODS OF NO_X EMISSION

There are two ways of low emission combustion processes leading to reduce pollutants reacting on environment. The so-called “primary methods” are used inside combustion chamber. The ”secondary methods” of reducing of the emissions are realised outside the combustion chamber along the cold duct of flue gases. The “primary methods” are used especially in internal combustion engines, gas turbines, a small gas and oil boilers and other kinds of burners. The most important factors, which can be modified during combustion processes are temperature, air excess ratio, air and natural gas streams, combustion aerodynamic or reduction quality of rich flame. The choice of these factors depend on required reduction efficiency, level of NO_x emission, fuel nitrogen, kind of fuel, combustion temperature and type of furnace [4].

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2.1. “Primary methods”

– *Air graduation in combustion process.* There are two stages of the low emission combustion using the air graduation. The first one goes with air excess ratio $\lambda = 0,5 \div 0,8$. A lot of radicals (e.g. $HCN\cdot$, $CH_i\cdot$, $NH_i\cdot$) are formed in this rich zone. It is advisable to limit the transformation of HCN and NH_3 to NO. It would be better that HCN i NH_3 transformed to N_2.

The second stage proceeds in combustion zone when the secondary air is injected in such way that $\lambda > 1$ known as reburning zone. The poor zone is formed to reburn CO, soot and carbon particles appearing in first stage of combustion. The presence time and temperature of reacting agents influence on NO reduction e.g. 4 s in reacting zone reduces NO_x to 50% [6].

The NO_x reduction can be effective when the primary and secondary air is well mixed causing better recycling of exhaust gases. Two geometrical parameters are important to reduce NO_x emissions. These are the number of burner nozzles and theirs distances from axes of the flame. The ring around the flame at the end of the burner is the best position of burner nozzle [5].

– *Reburning – graduating of fuel and air*. Reburnig is a method with many stages. Fuel is given twice and air is given three times inside the combustion process. The first stage leads to fuel combustion with an air excess ratio $\lambda = 1.05 \div 1.2$ depending on kind of fuel. The concentration of NO_x comes from nitrogen fuel and conditions of combustion processes. In this part most of fuel is burnt giving c.a. 80% of total chemical energy of fuel. In the second stage the additional fuel is given, known as reburning fuel, creating the reduction atmosphere with the chemical compounds and reduction radicals as HCN, NH_i i CH_i transforming NO to N_2 decreasing NO_x concentration. The natural gas and light oil are the most popular reburning fuels. In the third stage the air with a little excess (up to $\lambda = 1.2$) is given to reburn nonoxidized combustion products as CO. A lot of important factors as velocity, local temperature and temporary compounds of reacting substances, location of flame zone, position of nozzles and many others demand to be controlled continuously [7, 8]. Reburning is frequently applied in coal combustion processes.
– *Air control in the combustion processes*. The concentration of NO_x mainly depends on an air excess ratio for natural gas combustion. The concentration of NO_x increases with increasing of the air excess ratio and theirs maximum is found for no preheated air at the $\lambda \approx 1.1$. Whereas applied preheated air up to 1000 ^{o}C, the maximum of NO_x is obtained for $\lambda \approx 1.3$. It is possible to reduce NO_x up to 30% by increasing the air excess ratio $\lambda \approx 1.1$, while the preheated air is used up to high temperature [5, 9, 10]. When $\lambda > 1.1$ and no preheated air is applied NO_x decrease in the exhaust.
– *Flue-gas recirculation*. This method is based on the recirculation of flue gas and putting them inside the flame. Recirculation of flue gas causes the decreasing the temperature of the flame and local oxygen concentration in the flame, reducing NO_x concentration. The external recirculation of flue gas is a recycling of the part of flue gas by the other pipe from combustion chamber to the pipe with air combustion. This method is effective, but the additional equipments are needed as ventilators for cooled flue gas or injectors for high temperature flue gas. If the injector is situated inside the burner, then flue gas will be recirculated directly from combustion chamber [5]. It is possible to obtain 70% reduction of NO emission for 15–20% recycled flue gas when no preheated air is used [10]. The internal recirculation is caused by gas dynamics of the flame inside the combustion chamber. The recirculated flue gas is taken directly from the environment of the burner to the flame. The most effective way to decrease

temperature of the flame is mixing of the main part of the recirculated flue gas with an air combustion at the area with no maximum temperature found [13]. GAFT and FLOX burners are designed using this application [10–15].

2.2. ”Secondary methods”

The “secondary methods” are very effective, but they demand high financial costs e.g. new investments or using. Therefore they are applied when the “primary methods” are not sufficient enough to reduce NO_x. The most applied method is the selective catalytic reduction method (SCR). This is a dry method using ammonia as reduction gas at the presence of catalyst leading to transformation of NO_x to N_2 and H_2O. The condition takes place at temperature between 150 and 400 ºC depending on activity of used catalyst [16]. The noble metals (Pt, Pd, Rh) and transition metal oxides (V_2O_5, TiO_2, MoO_3) are used as the catalysts.

Fundamental problem of natural gas combustion is the presence in the flame of the pollutants, especially NO_x. One of the methods to reduce the NO_x concentration is the recirculation of flue gas. It is an effective and low cost primary method.

This paper is to investigate the natural gas combustion with recirculation of flue gas. The emissions of nitrogen oxides were investigated in depending on volume flow of recycled flue gas, applied nozzles and air excess ratio.

3. EXPERIMENTAL PROCEDURES

The experiments were performed with combustion reactor presented in Figure 1.

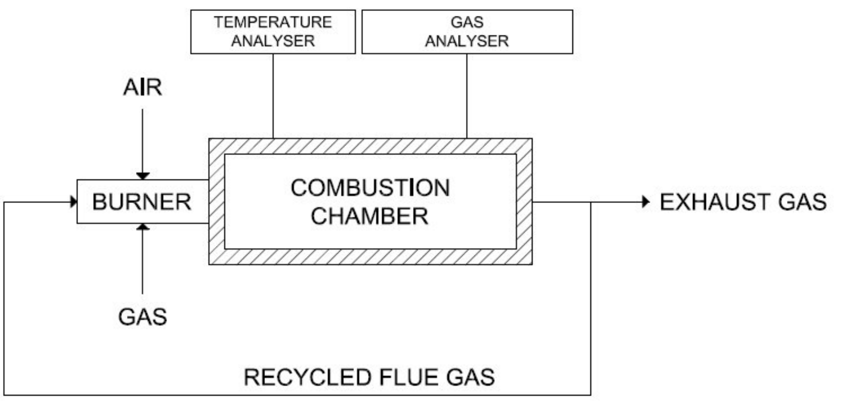

Fig. 1. *Experimental apparatus*

The experimental apparatus was composed of the combustion chamber with a “special designed” burner, gas and temperature analyser, recirculation of flue gas. The flow rates of air, gas and recycled flue gas were measured by rotameters.

The combustion reactor was composed of a “special designed” burner and the combustion chamber. The combustion chamber, made of heat-resisting steel, had a length of 1310 mm and a diameter of 160 mm. The thermal insulation of the combustion chamber was made of ceramic fibre whose thickness was 150 mm. The "special designed" burner was "pipe-in-pipe" type. Internal diameter was 34 mm and external diameter was 47 mm (Fig. 2). Fuel and air were mixed between two pipes. Next, fuel-air mixture flew by hole system to internal part of the burner, where it was mixed with cooled, dried exhaust gas. Three different nozzles were used in the experiments (diameters were D1 = 34 mm, D2 = 27 mm and D3 = 17 mm).

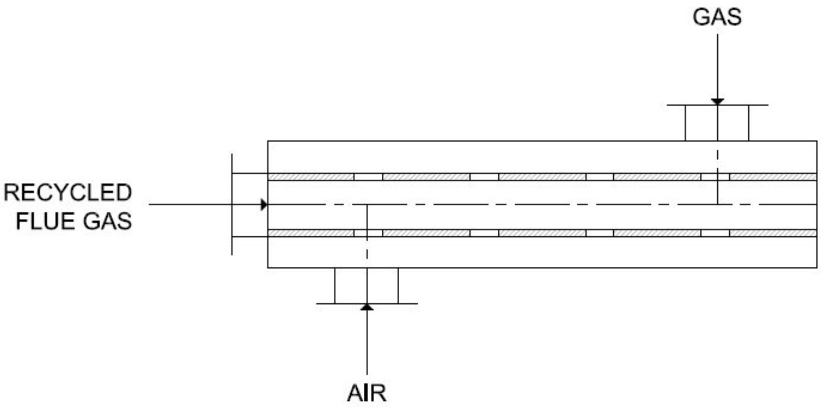

Fig. 2. *Scheme of a "special designed" burner*

Thermocouples were fitted at two different places along the chamber wall. The flame temperature was measured by a PtRh10-Pt coated thermocouple behind the burner. The exhaust temperature profile was measured by NiCr – NiAl coated thermocouple fitted at the exhaust sonde.

The investigated fuel was natural gas (GZ-50 with a high content of methane) taken from the city gas system. The composition of natural gas was 96% CH_4, 1,2% C_2H_6, 0,4% C_3–C_6, 2% N_2, 0,4% CO_2. The exhaust gas was measured by TESTO analyser (O_2, CO, NO, NO_2, SO_2, C_xH_y) and by gas chromatography method Agilent Technologies GC (CO, CO_2, C_XH_Y, O_2, N_2). The experimental parameters of studied process are given in Table 1.

Table 1. The experimental parameters of studied process

$\dot{V}_{gas}$	$\dot{V}_{exhaust}$	R	T_{flame}	$T_{exhaust}$
m^3/h	m^3/h	%	^oC	^oC
6,5–7,5	0–0,5	0–7,04	~1010	700–850

4. RESULTS

Figures 3–5 present the emission of nitrogen oxides depending on the recirculation ratio and applied nozzles for different air excess ratio ($\lambda = 1.16$; $\lambda = 1.25$; $\lambda = 1.34$). The investigated data of NO_x concentration were calculated taking into account the obligatory standards (O_2 = 3%).

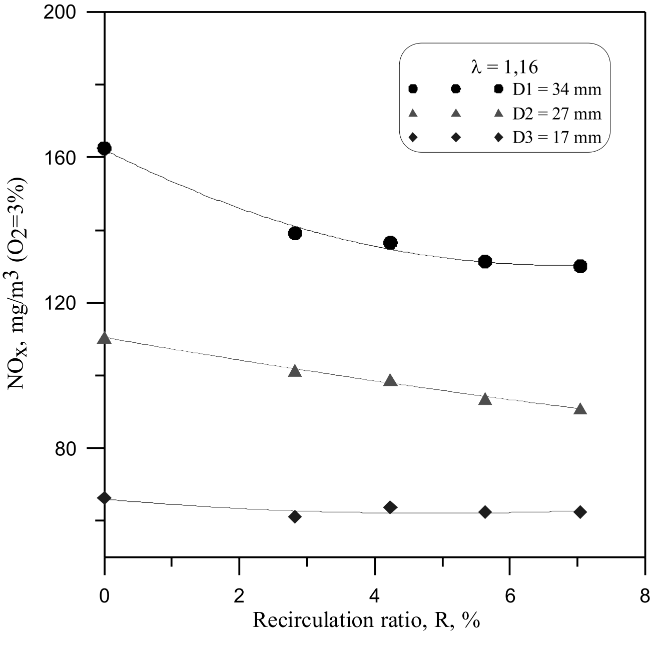

Fig. 3. *NO_x emission as a function of the recirculation ratio and applied nozzles for λ = 1.16*

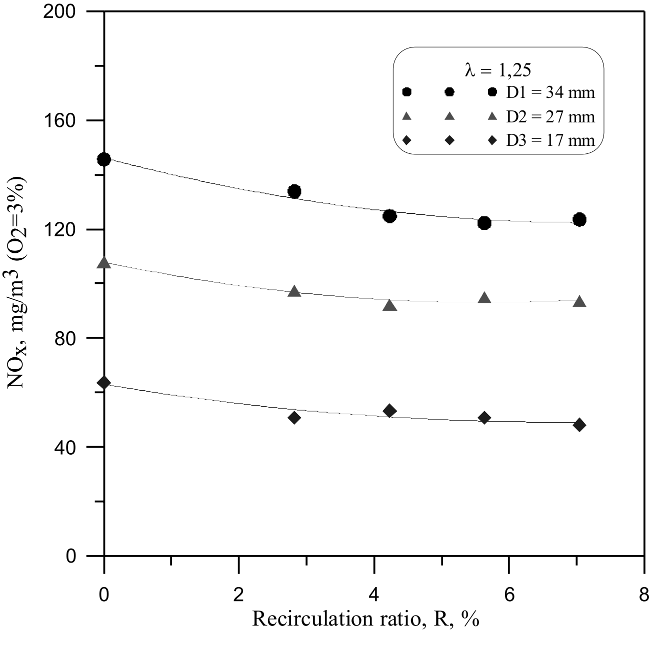

Fig. 4. *NO_x emission as a function of the recirculation ratio and applied nozzles for λ = 1.25*

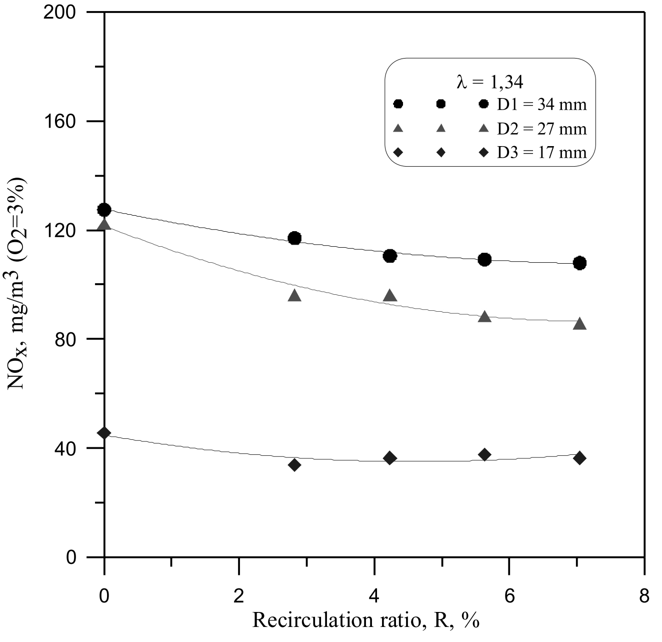

***Fig. 5.** NO_x emission as a function of the recirculation ratio and applied nozzles for λ = 1.34*

The external recirculation of flue gas on NO_x emission was investigated in the flame of natural gas in the combustion process conducted in the combustion chamber with a "special designed" burner. The recirculation of flue gas to combustion chamber reduces the flame temperature and local concentration of oxygen leading to NO_x decrease.

For all applied nozzles a maximum of NO_x concentration, for no recycled flue gas process, was observed. Taking into account the air excess ratio a maximum of NO_x concentration was observed for λ = 1.16. Close to three times lower NO_x concentration was observed comparing investigated results obtained for D1 = 34 mm and D3 = 17 mm (from 162.5 mg/m^3 up to 62.5 mg/m^3 for λ = 1.16). Due to the increasing of recycled flue gas, NO_x concentration was decreasing. Although the general tendencies decreasing of NO_x emission with increasing of the recirculation ratio was observed for all investigated applied nozzles, the best results were observed for the biggest applied nozzle (D1 = 34 mm). Increasing of recirculation ratio was not significant for the smallest applied nozzle (D3 = 17 mm). Comparing the NO_x emission received for application of recirculation of flue gas and without, only a little changes of NO_x emission were observed.

The most steady results were obtained for D1 diameter nozzle suggesting the steady operating conditions of the burner. The smallest applied nozzle, influenced the internal recirculation of flue gas to the flame, causing gasdynamics of the flame in the combustion chamber.

5. CONCLUSIONS

To conclude:

1. A maximum of NO_x concentration was observed for the air excess ratio $\lambda = 1.16$ for three different applied nozzles. NO_x was decreasing when higher air excess ratio applied.
2. 40% higher NO_x concentration was observed for D1 = 34 mm compare to D3 = 17 mm.
3. Recirculation of flue gas influences on the NO_x concentration.
4. NO_x concentration was decreasing with an increasing recirculation ratio for all applied nozzles.
5. The most significant influence of recirculation ratio on NO_x concentration was observed for nozzle of diameter D1 = 34 mm.
6. NO_x concentration was not significant for all applied recirculation ratios in the case of nozzle D3 = 17 mm.
7. The steady operating conditions of the burner were obtained for nozzle of D1 diameter.
8. The smallest applied nozzle of D3 = 17 mm causes the internal recirculation of flue gas to the flame.

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REFERENCES

[1] *Birol F.*: World Energy Outlook 2009, International Energy Agency, AGH, Kraków (2009)

[2] *Wilk R.K.*: Low-emission combustion, Wyd. Politechniki Śląskiej, Gliwice (2002)

[3] *Tomeczek J.*, *Góral J.*, *Gradoń B.*, *Sitko J.*: The influence of combustion conditions on NO_x emission in natural gas diffusion industrial flame, Hutnik – Wiadomości Hutnicze, 59 (1992) 8, 262–265 (in Polish)

[4] *Kordylewski W. i in.*: Low emission combustion techniques in power industry, Oficyna Wyd. Politechniki Wrocławskiej, Wrocław (2000) (in Polish)

[5] *Tomeczek J.*: Primary methods of NO_x emission reduction from industrial furnaces in natural gas combustion, Hutnik – Wiadomości Hutnicze, 61 (1994) 7, 235–238 (in Polish)

[6] *Bartok W.*, *Sarofim A.F.*: Fossil fuel combustion. A source book, John Wiley and Sons Inc., New Yourk, Chickester, Brisbane, Toronto, Singapur (1991)

[7] *Kordylewski W.*, *Rybak W.*, *Salomon A.*: Efficiency of NO emission reduction by reburning method during gas, liquid and fossil fuels combustion, III Sympozjum nt. Ograniczania emisji zanieczyszczeń do atmosfery, Szklarska Poręba (1996) (in Polish)

[8] *Seo A.*, *Hase K.*: Study on NO_x reduction in reburning, Combustion Science and Technology, 131 (1998) 381–393

[9] *Tomeczek J.*: Possibility of nitrogen oxides emission reduction from industrial furnaces in natural gas combustion, Gospodarka Paliwami i Energią, 3 (1994) 2–4 (in Polish)

[10] *Gradoń B.*: Ecological aspects of nitrogen oxides emission in combustion proceses, Ochrona środowiska a aglomeracje wielkoprzemysłowe – Informator specjalistyczny branży ekologicznej, 4 (2007) 24–31 (in Polish)

[11] *Wünning J.G.*: FLOX – Flameless Combustion. Thermoprocess Symposium (2003), VDMA

[12] *Wünning J.A.*, *Wünning J.G.*: Flameless oxidation to reduce thermal NO-formation, Progress of Energy Combustion Science, 23 (1997) 81–94

[13] *Tomeczek J.*, *Góral J.*, *Gradoń B.*: Low emission NO_x from a natural gas diffusion burner, Gospodarka Paliwami i Energią, 2 (1996) 2–4 (in Polish)

[14] *Tomeczek J.*, *Góral J.*, *Gradoń B.*: Low emission burner for radiant tubes, Hutnik – Wiadomości Hutnicze, 64 (1997) 8, 211–215 (in Polish)

[15] *Tomeczek J.*, *Ochman J.*, *Góral J.*: Low emission burner for flat flame burner for high temperature furnaces, Hutnik – Wiadomości Hutnicze, 74 (2007) 9, 265–269 (in Polish)

[16] *Kuropka J.*: Denitriding of exhaust gases – actual condition and development prospects, Ochrona środowiska, 1 (1995) 19–24 (in Polish)

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