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AN EXPERIMENTAL AND NUMERICAL STUDY OF THE INFLUENCE OF FGR ON NO_X FORMATION

EKSPERIMENTALNA IN NUMERIČNA ŠTUDIJA VPLIVA FGR NA TVORBO NO_X

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In many countries NO_x emissions are limited because of their adverse impact on the environment. Different methods to reduce the amount of NO_x released into the environment from combustion devices have been developed. The main technique to prevent NO_x formation in accordance with the regulation limit at a reasonable cost is flue-gas recirculation (FGR). This paper presents the results of laboratory tests to determine the emissions of nitrogen oxides from a standard natural-gas-fired burner. There was a marked effect on the NO_x emissions by varying the excess air and the quantity of recirculated flue gases in the combustion air. A significant reduction in the NO_x, by approximately 80%, was achieved by external flue-gas recirculation. The results obtained from the measurements were compared with those obtained from a calculation of the equilibrium compositions and the adiabatic flame temperature of the combustion products related to the quantity of supplied combustion air and recirculated flue gases.

Keywords: flue-gas recirculation (FGR), nitric-oxide reduction, standard industrial burner

V številnih državah je emisija NO_x omejena zaradi škodljivega vpliva na okolje. Razvite so bile različne metode za zmanjšanje NO_x, emitiranega v okolje iz zgorevnih naprav, in najvažnejša metoda za preprečenje tvorbe NO_x, skladno s predpisi in za sprejemljivo ceno je recirkulacija zgorevnih plinov (FGR). V tem članku predstavljamo rezultate serije laboratorijskih preizkusov, namenjenih ugotavljanju emisije dušikovih oksidov iz standardiziranega gorilnika za zemeljski plin. Emisija NO_x je močno odvisna od prebitka zraka in od količine recirkuliranih zgorevnih plinov v zraku za zgorevanje. Pomembno zmanjšanje NO_x, približno 80 %, je bilo doseženo z eksterno recirkulacijo zgorevnih plinov. Eksperimentalno določene vrednosti so bile primerjane s tistimi, ki so bile izračunane na osnovi ravnotežne sestave in adiabatske temperature plamena v odvisnosti od količine zgorevnega zraka in recirkuliranih zgorevnih plinov.

Ključne besede: recirkulacija zgorevnih plinov (FGR), redukcija dušikovih oksidov, standardni industrijski gorilnik

1 INTRODUCTION AND OBJECTIVES

In gaseous hydrocarbon combustion, the formation of nitrogen oxides is primarily the result of the high-temperature reaction of the molecular nitrogen in the air (and possibly in the gas) and the combustion oxygen. There are three kinds of nitrogen oxides: nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O). NO_2 and N_2O have the most damaging impact on the atmosphere. Gas-fired furnaces and boilers produce mainly NO, but in contact with the air, the NO gradually oxidizes into NO_2.

There are three mechanisms for the formation of NO_x in combustion processes: thermal-NO_x, prompt-NO_x and fuel-NO_x [1,2]. Thermal-NO_x is formed from molecular nitrogen at very high temperatures (>1000 °C). Prompt-NO_x is formed in fuel-rich regions, where hydrocarbon radicals react with molecular nitrogen to form NO_x at high temperatures. However, the possibility of prompt-NO_x is usually negligible, because industrial furnaces mostly run under oxygen-rich conditions. Fuel-NO_x is formed from nitrogen atoms bound in the fuel. Accordingly, the gaseous fuels generate almost exclusively thermal-NO_x, with very little prompt-NO_x and fuel-NO_x, because gaseous fuel does not contain bound nitrogen, unlike liquid or solid fuels. The nitrogen present in the gas is molecular (N_2) and behaves like the nitrogen in air. It generates no fuel-NO_x.

The most important factors in thermal-NO_x emission can be expressed by the formula for NO formation [3]:

$$[NO] = K_1 \exp(-K_2/T) \cdot [N_2] \cdot [O_2]^{1/2} \cdot t \qquad (1)$$

where K_1 and K_2 are constants, T is the temperature and t is the time.

In premixed systems, controlled by the Zeldovich mechanism, temperature, composition and time are the important variables determining NO_x emissions. The following measures can be taken to reduce NO_x emissions from a furnace:

- Decrease the flame volume at high temperatures because temperature is an exponential factor;
- Minimize the oxygen concentration;
- Shorten the residence time of the N_2 and O_2 molecules at high temperatures.

While temperature is the most important factor for gaseous fuels, there are a number of different techniques involved in NO_x reduction:

- Lowering the flame temperature (<1400 °C);
- Lowering the oxygen concentration in the reactive medium,

- Lowering the residence time by increasing the turbulence.

The techniques for reducing NO_x emissions involve: flue-gas recirculation, fuel staging, as well as reburning and lean-burn combustion (>1400 °C) and post-combustion techniques such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). The first two are by far the most widely used in industry because they prevent NO_x formation in accordance with the limit of the regulation at a lower cost, which is acceptable to manufacturers. These technologies have, in all cases, been developed to reduce temperature peaks in oxygen-rich parts of the flame.

By recirculating part of the flue gases (15 % to 20 %), NO_x emissions can be significantly reduced. The injection of the flue gases increases the ballast of the gases not involved in combustion, thereby lower the flame temperature. A portion of the product gases leaving the combustor is sent back to the inlet combustion air. When this effective process is applied to an atmospheric furnace flame it is called flue-gas recirculation (FGR). The recirculation can be performed either by recycling the flue gas from the exhaust of the combustor by mechanical means (external FGR) or by entraining the product gases from the combustion zone by high-velocity air or fuel jets (internal FGR).

External FGR is the most widespread technique in industry. Part of the flue gases is re-injected in the burner or mixed with the combustion air by means of a high-temperature fan and control system. This technique can lower NO_x by a factor of two, and by adjusting the flue-gas recirculation rate (15 % to 20 %) NO_x can, in any case, be brought below 100 mg/m^3 [3]. The main reduction is in thermal-NO_x. Because of the high activation energy of the thermal-NO_x mechanism, due to the strong triple bond in the N_2-molecule, any scheme that suppresses peak temperatures will lower the NO_x output. It would be beneficial to inject an inert gas, such as nitrogen, or water, which both act as diluents, lowering the local oxygen concentration and whose additional heat capacity lowers the peak temperature. For this purpose, exhaust gases are reasonably inert. The effect of high CO_2 and H_2O levels in the flue gas is to increase the specific heat capacity of the burned gases for a given quantity of heat release, thus lowering the operating temperatures. Recycled gas can be supplied to the burners or added to the combustion air. Since thermal-NO_x is the primary source of NO_x formation from natural gas and distillate oils, these fuels being generally low or devoid of nitrogen, this method is particularly successful with oil- or gas-fired burners.

The influence of flue-gas recirculation on the NO_x emissions from turbulent jet flames has been extensively studied, and recent research results can be found in several references. Experimental results [4] demonstrate that FGR can be used in the case of reheating furnaces in steel plants to reduce NO_x formation when the emission standard cannot be met by operational adjustments. The paper[5] presents an experimental and numerical study of the effect of FGR on flame characteristics and pollutant emissions performed in a small-scale laboratory furnace fired by an industrial type gas-swirl burner. NO_x was reduced to 25 μg/g for pulse-combustion hot-water boilers [6]. The optimal combinations of the preheated air temperature and oxygen concentration have been predicted in the case of FGR, which could provide the highest possible temperature in the furnace, while keeping the NO_x emission lower than the permitted value [7]. The combination of air preheating and FGR not only improves the combustion efficiency, but also suppresses NO_x emission in the combustion process [8]. Modern, low-NO_x domestic oil and gas burners use the effect of flue-gas recirculation to lower the combustion temperature and hence to reduce the amount of NO formed [9]. In order to reduce NO_x emission, FGR applied to midsize power plants is discussed [10].

The objective of this work was to investigate the effect of flue-gas recirculation on the pollutant emissions of nitrogen oxides adjusting the air-to-fuel ratio and the quantity of the recirculated flue gases in the combustion air. A standard industrial non-premixed turbulent burner using natural gas is considered as a candidate for implementing strategies for the control of the pollutant emissions.

2 EXPERIMENTAL FACILITY

The test combustion facility and instrumentation that were used as the experimental model for the investigation of the effect of external recirculation of the flue gases and the excess air on the NO_x are shown in **Figure 1**. The combustion-chamber volume is insulated with a refractory concrete insulation. In **Figure 2** the principle scheme of the standard industrial non-premixed turbulent low-NO_x burner designed for a total maximum heat input of 100 kW is presented. The whole combustion air enters the burner chamber through the air nozzles inclined to the axis of symmetry of the gas gun. With inclined natural gas nozzles, related to the air nozzles, a stabilized flame is achieved in order to realize a smaller reaction

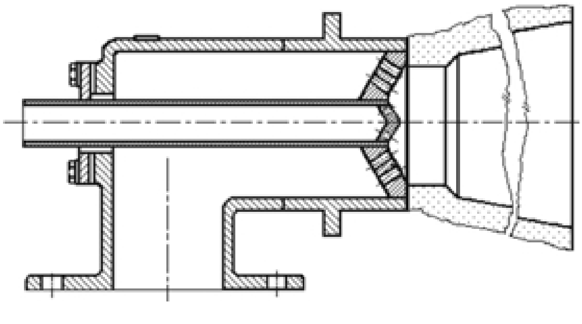
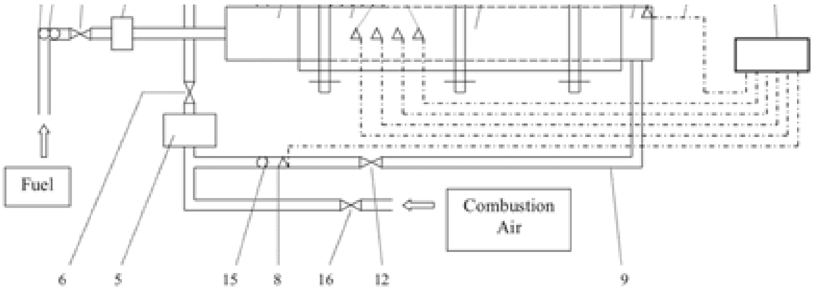


Figure 1: Turbulent low NO_x burner of 100 kW
Slika 1: Turbulentni gorilnik 100 kW z nizkim NO_x



1 – COMBUSTION CHAMBER, 2 – EXTENT OF COMBUSTION CHAMBER, 3 – BURNER, 4 – REFRACTORY LINING, 5 – BLOWER, 6 – REGULATING VALUE FOR AIR, 7 – GAS FLOWMETER, 8 – THERMOCOUPLES, 9 – RETURNED FLUE PIPE, 10 – TEMPERATURE MEASURING, 11 – STATIC PRESSURE MEASURING, 12 – REGULATING COCK OF RETURNED FLUES, 13 – REGULATING VALUE FOR GAS, 14 – JOIN OF ANALYZER TESTO 33, 15 – JOIN OF ANALYZER TESTO 325, 16 - THROTTLE, 17 – RECORDING DEVICE COMET MS 3, 18 – JOIN ON RECORDING DEVICE

Figure 2: Experimental scheme of the test combustion facility with measuring equipment
Slika 2: Eksperimentalna zgorevna naprava z merilno opremo

zone. The reactive zone of the burner covers only a very small part of the volume of the combustion chamber because normally the main parts of the reactions take place within the burner chamber and the nearly-burned-out flue gas enters the combustion chamber where the remaining reactive components will react.

The temperature of the flue gases was measured with thermocouples at six points in the near-burner region, at one point at the end of the combustion chamber, and in the return duct. The combustion-product samples were taken continuously using a multi-point stainless-steel probe. The major gas-phase species concentrations were detected by the chemical measuring cells in Testo flue-gas analyzers (Testo 33 and Testo 325) at the following positions: O_2, CO_2, CO and NO_x at the end of combustion chamber, O_2 and CO_2 in the return line, and O_2 and CO_2 before the burner in the mixture of fresh combustion air and flue gases. The temperatures and concentration readings were recorded over a period of approximately one hour of continuous operation under steady-state conditions with regard to the set values of the natural gas and the air supply varying the recirculating part of flue gases (FGR rate).

All the experimental investigations were made at a burner input of 51.58 kW, performed with natural gas as a fuel at a flow of 5.5 m^3/h and with non-preheated combustion air. The recirculated part of the flue gases in the mixture with the combustion air was varied between 0 % and 20 %. The value of the air-to-fuel ratio n was changed between values of 1.11 and 1.31.

3 EXPERIMENTAL RESULTS

The effectiveness of FGR depends on both, the quantity and temperature of the recirculated flue gases. In this case the experiments were performed with cooled, recirculated gas at temperatures of less than 300 °C.

The effects of varying the proportion of the flue gases, from the combustion chamber exit via a duct into the combustion air, and the quantity of excess air on the flue-gas temperature, at constant heat input using the standard natural-gas-fired burner operating with ambient combustion air, are shown in **Figure 3**. **Figure 4** shows

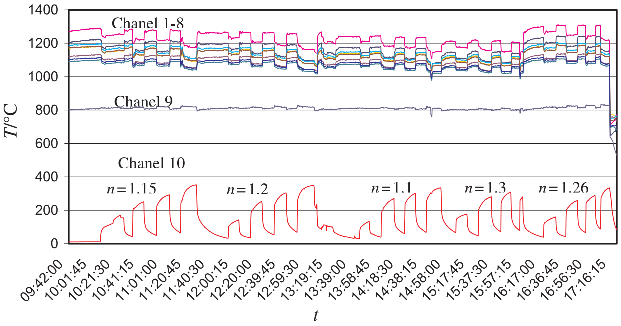


Figure 3: Effects of recirculated flue gases and excess air on the flue gas temperatures
Slika 3: Vpliv recirkuliranih zgorevnih plinov in prebitka zraka na temperaturo zgorevnih plinov

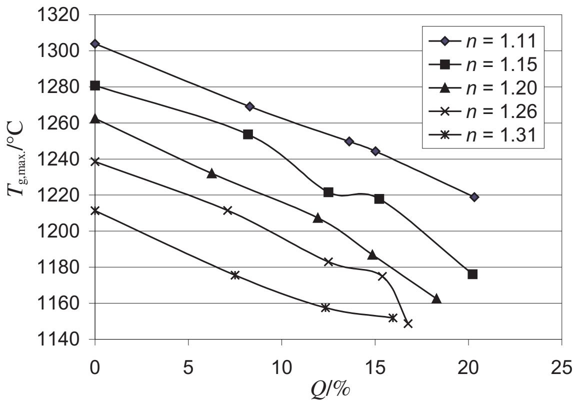


Figure 4: Effect of recirculated flue gases Q on the peak temperatures of flue gases measured in the combustion chamber
Slika 4: Vpliv recirkuliranih zgorevnih plinov Q na maksimalno temperaturo zgorevnih plinov, izmerjeno v zgorevni komori

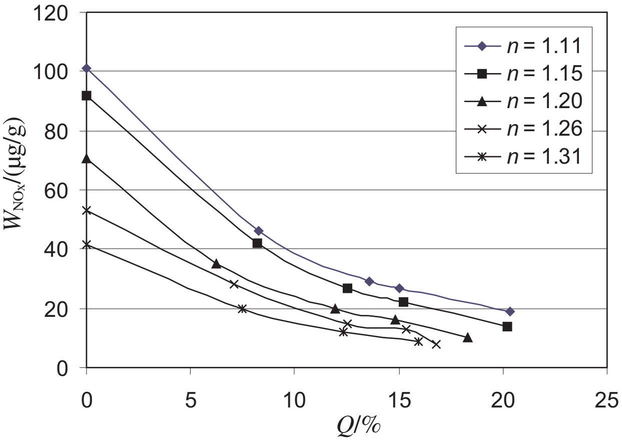


Figure 5: Effect of recirculated flue gases Q on NO_x formation
Slika 5: Vpliv recirkuliranih zgorevnih plinov Q na tvorbo NO_x

the influence of the quantity of recirculated flue gases in the combustion air and excess air on the peak temperature of the flue gases measured in the combustion chamber.

Figure 5 shows the effects of the quantity of supplied combustion air and the quantity of the recirculated gas on NO_x emission. It is shown that NO_x emissions without recirculation of the flue gases reach about 100 μg/g for fire operation at an excess air of $n = 1.11$. This is a relatively low emission due to the high fuel-flow rate, which reduces residence times (smaller flame) and the thickness of the above-mentioned flame regions. If the quantity of recirculating flue gases in the combustion air increases from 0 % up to 20 %, the actual NO_x values decrease. For fire operation at an excess air of $n = 1.11$, the decrease in NO_x emissions is approximately 80 %. It is known that natural-gas-fired industrial furnaces mostly run under this condition.

As indicated in the introduction's discussion of the Zeldovich mechanism in premixed systems, temperature, composition and time are the important variables determining NO_x emissions (Eqn. 1). These variables are also controlling in non-premixed flames; however, the composition varies from point to point in the flow and is governed by fluid mechanical mixing. In this case, the relatively high fuel-flow rate through the heat-release rate reduces the residence times and in this way reduces NO_x formation. Reduced residence times also allow the flames to be more adiabatic since less time is available for radiating losses to occur. However, according to the obtained experimental results the temperature decreases have a significant effect on NO_x formation.

Increasing the excess air level without recirculation of the flue gases shows a marked influence on the NO_x emissions. Increasing the excess air from 1.11 up to 1.31 causes a decrease in the actual NO_x values, and this is evidently due to the dilution effect. When increasing the excess air, NO_x emissions are observed to decrease by approximately 60 %. However, the reduction of NO_x emissions in this way, increasing the amount of excess air above the stoichiometric conditions, is not economically viable because it decreases the combustion efficiency.

4 NUMERICAL RESULTS

For the comparison of the measurement results with the theoretical data it was necessary to calculate the adiabatic temperature and the composition of the mixture at a given temperature, pressure and stoichiometry in order to find out the variation of the temperature and the combustion-product mixture composition with the quantity of recirculated flue gases.

For a combustion process that takes place adiabatically and with no work or changes in kinetic or potential energy, the temperature of the products is referred to as the adiabatic flame temperature. This is the maximum temperature that can be achieved for the given reactants, because any heat transfer from the reacting substances and any incomplete combustion would tend to lower the temperature of the products. The adiabatic temperature can be controlled with the amount of excess air used. This case of combustion in the test facility can be considered as a constant-pressure system. If a fuel-air mixture burns adiabatically at constant pressure, the absolute enthalpy of the reactants at the initial state (T_i = 298 K, p = 101325 Pa) equals the absolute enthalpy of the products at the final state ($T_i = T_{ad}$, p = 101325 Pa), i. e., the application of the first-law statement results in

$$H_{reac}(T_i, p) = H_{prod}(T_{ad}, p) \tag{2}$$

Eqn. 2 defines the constant-pressure adiabatic flame temperature.

The condition for equilibrium can be stated in terms of any of several thermodynamics functions, for example, the minimization of the Gibbs free energy or Helmholtz free energy, or the maximization of the entropy. If the temperature and pressure are used to characterize a thermodynamic state, the Gibbs free energy is the most easily minimized, because the temperature and pressure are its natural variables. In this consideration of chemical equilibrium the Gibbs function was introduced in calculating the equilibrium composition of ideal-gas mixtures using equilibrium-constants together with element conservation [1].

The combustion of methane (CH_4) in air for an initial temperature of methane of 292 K and combustion air at 290.5 K (the same values as during the experimental investigations), and at constant pressure of 101325 Pa, was considered. The Fortran program HPFLAME, which incorporates the Olikara & Borman equilibrium routines[2], to carry out the thermochemical calculations for the equilibrium compositions and the constant-pressure adiabatic flame temperature for various quantities of recirculated flue gases was used. The input file for the program requires the definition of the fuel by providing the number of carbon, hydrogen, oxygen, and nitrogen atoms constituting the fuel molecule, the equivalence ratio, a guess for the adiabatic flame temperature, the pressure, and the reactants' enthalpy.

The reactant-mixture enthalpy of the fuel, the air and the FGR was determined by the equation:

$$H_{\mathrm{reac}}/(\mathrm{kJ}) = N_{\mathrm{F}}\overline{h}_{\mathrm{F}} + N_{\mathrm{O_2}}\overline{h}_{\mathrm{O_2}} + N_{\mathrm{FGR}}\overline{h}_{\mathrm{FGR}} \tag{3}$$

The mass-specific enthalpy per unit mass of mixture is

$$H_{\mathrm{reac}}/(\mathrm{kJ/kg}) = \frac{H_{\mathrm{reac}}}{m_{\mathrm{reac}}} = \frac{H_{\mathrm{reac}}}{N_{\mathrm{F}}M_{\mathrm{F}} + N_{\mathrm{A}}M_{\mathrm{A}} + N_{\mathrm{FGR}}M_{\mathrm{FGR}}} \tag{4}$$

The molar specific enthalpy of the recycled gases is

$$\overline{h}_{\mathrm{FGR}}/(\mathrm{kJ/kmol}) = h_{\mathrm{FGR}}M_{\mathrm{FGR}} \tag{5}$$

The number of moles of FGR was obtained from the definition

$$N_{\mathrm{FGR}}/(\mathrm{kmol}) = (N_{\mathrm{F}} + N_{\mathrm{A}})\%\mathrm{FGR}/100\% \tag{6}$$

In the above equations m/(kg) is the mass, M/(kg/kmol) is the molar mass, N/(kmol) is the number of moles and h/(kJ/kg) is the enthalpy. The subscript A denotes the air, F the fuel, and reac the reactants.

The calculated equilibrium compositions and the flame temperature of the combustion products for the combustion of methane in air at an excess air of $n = 1.11$ are plotted against the various quantities of recirculated flue gases (the same values as during the experimental investigations) in **Figure 6-7**, respectively. This is only a schematic illustration because the temperature and composition distributions are determined by fluid mechanical, chemical-kinetic and thermal effects.

Figure 6 shows how the theoretical composition of the furnace gases varies with the quantity of recirculated flue gases. Some of the minor species of equilibrium combustion, such as the O atom and the diatomic species OH and NO, are shown. The atoms N and H are not presented because their levels are below 100 µg/g and 1 µg/g, respectively. Thermal NO is produced primarily in flame regions that have simultaneously high temperatures and high concentrations of O and OH atoms, i.e., conditions near to stoichiometry. Accordingly, the O and OH maxima have implications for the kinetics of NO formation. The level of the hydroxyl radical OH is more than an order-of-magnitude greater than the O atom. On the other hand, N-atom concentrations are several orders-of-magnitude lower than those of the O atoms. The lack of dissociation of the N_2 molecule is a result of the strong triple covalent bond. The NO concentration falls rapidly with the quantity of recirculated flue gases, as illustrated by the curve shown in **Figure 6**.

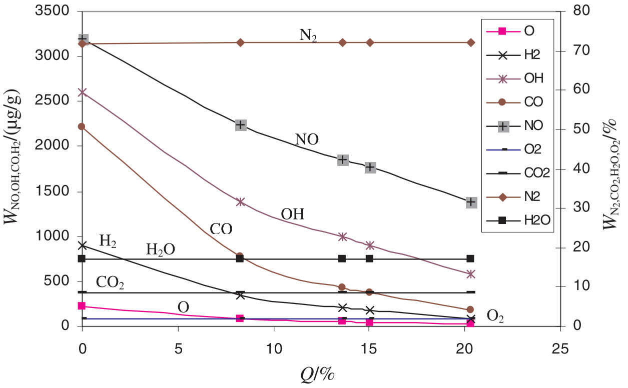


Figure 6: Equilibrium composition of product species for methane combustion at n = 1,11 and various quantity of recirculated flue gases Q

Slika 6: Ravnotežna sestava zgorevnih produktov pri zgorevanju metana pri n = 1,11 in pri različni količini recirkuliranih zgorevnih plinov Q

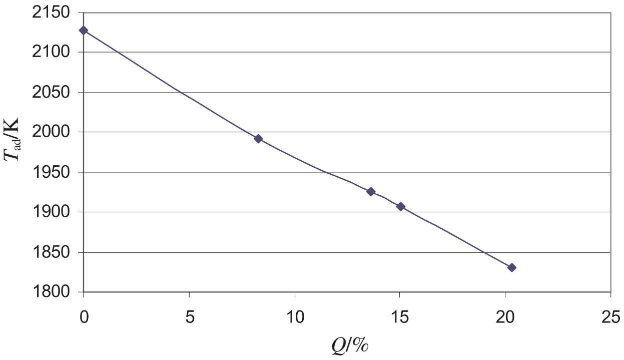


Figure 7: The constant-pressure adiabatic flame temperature T_{ad} for methane combustion at n = 1,11 and various quantity of recirculated flue gases Q

Slika 7: Adiabatska temperatura plamena T_{ad} pri zgorevanju metana pri konstantnem tlaku pri n = 1,11 in pri različni količini recirkuliranih zgorevnih plinov Q

As it can be seen from **Figure 7,** the quantity of recirculated flue gases has a pronounced effect on the adiabatic flame temperatures, resulting in a drop of about 320 K from the zero recycle condition with 20 percent of the recirculated flue gases. Consequently, such temperature decreases have a significant effect on NO_x formation.

5 CONCLUSIONS

Advances made with standard burners have succeeded in lowering NO_x emissions to levels below 200 mg/m³ for natural gas, without using any special techniques. The lowering emissions' thresholds to 100 mg/m³ or less, would lead to the development of low-cost technologies for further lowering the levels of oxides of nitrogen. The two most popular techniques are waste-gas recirculation and fuel staging.

The results of this study provide useful independent information about the practical limits of flue-gas emissions that are achievable using a standard industrial low-NO_x burner and advanced techniques for reducing NO_x emissions. We have demonstrated that external flue-gas recirculation can be used safely and effectively with an existing burner and that significant reductions in NO_x emissions of approximately 80 % are possible, without significant effects on flame stability and the overall combustion efficiency.

The marked reduction in the NO_x and CO values is in the region of the FGR rate from 0 % up to 10 %. Taking into consideration the amount of reductions in the emission and, on the other hand, the lowering of combustion efficiency because of the decrease of the operating temperatures, the optimum value of the FGR rate is between 10 % and 15 %. The measurement and experimental results confirm that the decrease in NO_x emissions is due, primarily, to the flame temperature reduction.

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6 REFERENCES

[1] J. Warnatz, U. Mass, R. W. Dibble, Combustion, Springer- Verlag Berlin Heidelberg New York, 1996, 41–43

[2] S. R. Turns, An introduction to combustion, McGraw-Hill, 2nd ed., 2000, 52–65

[3] L. Scrive, Reduction of pollution during combustion in gas-fired process boilers, INFUB, Lisbon 1995, 198–205

[4] H. S. Teng, T. S. Huang, Control of NO_x emissions through combustion modifications for reheating furnaces in steel plants, Fuel, 75(**1996**)2, 149–156

[5] J. Baltasar, M. G. Carvalho, P. Coelho, M. Costa, Flue gas recirculation in a gas-fired laboratory furnace-measurements and modelling, Fuel, 76(**1997**)10, 919–929

[6] Y. Michel, F. E. Belles, Effects of flue-gas recirculation on NO_x production and performance of pulse combustion hot-water boilers, Combustion Science & Technology, 94(**1993**)1–6, 447–468

[7] J. Yuan, I. Naruse, Modeling of combustion characteristics and NO_x emission in highly preheated and diluted air temperature, International Journal of Energy Research, 22(**1998**)14, 1217–1234

[8] H. S. Guo, Y. G. Ju, K. Maruta, T. Niioka, J. Sato, Numerical study of NO_x emission in high temperature air combustion, JSME International Journal Series B-Fluids & Thermal Engineering, 41(**1998**)2, 331–337

[9] H. Dreher et al., Numerical simulation of the oil combustion process in a 100 kW serially produced low NO_x combustion system, Combustion Science & Technology, 121(**1996**)1–6, 235–253

[10] G. Vermes, L. E. Barta, J. M. Beer, Low NO_x emission from an ambient pressure diffusion flame fired gas turbine cycle (APGC), Journal of Engineering for Gas Turbines and Power-Transactions of the ASME, 125(**2003**)1, 46–50