Reduction of NOx formation under the limit combustion conditions through the application of combined primary deNOx methods on the gas boilers

Miroslav Rimár[1], Marcel Fedák[1], Andrii Kulikov[1], Ivan Čorny[1], Milan Abaham[1] and Ján Kizek[2]

The article deals with the issue of reducing the formation of nitrogen oxides in the boundary conditions of combustion. These conditions occur at a high thermal load of the combustion chamber, while the amount of nitrogen oxides increases exponentially according to the Arrhenius formula. Due to this, special attention must be paid to the combustion of natural gas, especially because there is a constant demand for minimizing the formation of pollutants. The simulation model of a steam boiler with 4 industrial gas burners (heat output of each is 17.8 MW) and the high thermal load of the combustion chamber (0.59 MW.m-3) is presented in the paper.

Simulation modelling and subsequent experimental measurements on a real object show how classical primary de-NOx methods manifest themselves under extreme thermal loads. The result of the research is a significant reduction in NOx production, which was achieved by a combination of primary methods.

Keywords: combustion, boiler, ANSYS, pollutants, NOx.

Introduction

Optimizing of combustion processes is an important task, considering efficient energy production. An important area is the combustion of natural gas under the limiting/boundary conditions of the thermal load in the combustion chamber, which relates directly to the formation of nitrogen oxides. There are many scientific papers (Zeldovic 1947, Gurevich 1975, Segal 1966) which describe the mechanisms of NOx formation in the combustion process, as well as articles on the chemical kinetics of combustion (Semenov 1930) and flame heat relation to NOx formation (Fenimore 1972, Chen 2017).

As far as the combustion process itself is concerned, it is important to emphasize that high flame temperatures are an integral part of combustion and are critical parameters in terms of burner or boiler performance, as well as flame stability and heat transformation stability (Rimar 2014). Flames are more stable and more homogeneous when the combustion air is preheated compared to normal air temperature (Gopalokrishnan 2007, Lamoreux 2010).

Combustion in the thermal load limiting conditions of the combustion chamber is characterized by an extreme thermal load of the combustion chamber (ETLCCh). The extreme heat load of the combustion chamber means that there is a high temperature in the combustion chamber; this has a negative impact on the formation of nitrogen oxides (Glarborg 1995, Yeh 2013, Rimar 2014, Durdán and Kostúr, 2015).

According to the published works (Fackler 2015, Horbaj 2005, Yeromin 2018), the flame temperature is one of the most important factors influencing the formation of NOx. A particularly critical situation of NOx formation occurs under limiting combustion conditions. Since it is one of the European Union's objectives to alleviate the impact of human activity on the quality of the environment (Hayhurst 1980), the reduction of the formation of nitrogen oxides in the combustion devices is very actual (SR legislation 252/2016). According to European Union legislation, emissions of nitrogen oxides must be significantly reduced (SR Regulation 442/2013).

Recent findings point to the flame geometry as an effective factor in influencing flame temperature and flue gas presence time in the boiler combustion chamber (Basu 1999, Anderson 1995, Panda 2011, Xubo 2016, Duplakova 2014). By setting the flame geometry, it is possible to minimize zones with a temperature above 1775 K, which is limiting in terms of the exponential growth of nitrogen oxides. According to Holoubek (2002) and Rimar (2016), the geometry of the flame is one of the essential factors affecting the formation of nitrogen oxides during combustion.

1.1 Nitrogen oxides formation

Total NOx emissions in the flue gas of steam boilers can be divided into two main compounds NO and NO_2 (Miller 1996, Ferstl 2011, Flimel 2010, Jandačka 2015). Approximately 95-99% of NOx is NO, while the

---

[1] *Miroslav Rimár, Marcel Fedák, Andrii Kulikov, Ivan Čorny, Milan Abaham:* Department of Process Technique, Faculty of Manufacturing Technologies of the Technical University of Kosice with a seat in Prešov, Bayerova 1, 080 01 Prešov, Slovak Republic, miroslav.rimar@tuke.sk, marcel.fedak@tuke.sk, andrii.kulikov@tuke.sk, ivan.corny@tuke.sk, milan.abraham@tuke.sk

[2] *Ján Kizek,* Department of Thermal Technology and Gas Industry, Institute of Metallurgy, Faculty of Materials, Metallurgy and Recycling of the Technical University of Košice, Letná 9, 042 00 Košice, Slovak Republic, jan.kizek@tuke.sk

content of more toxic NO_2 is not more than 1-5%. Under the influence of natural factors, the largest part of NO after exhaust to the atmosphere is converted to NO_2. Therefore, the calculation of the NOx mass concentrations and emissions is carried out according to NO_2.

Thermal NO - the concentration of thermal NO is controlled by the molar concentrations of nitrogen and oxygen and the combustion temperature. Such processes have a high energy consumption of 561 kJ/mol and thus are dependent on the overall process temperature.

The required time for combustion of the methane/air mixture is approximately 10^{-2} to 10^{-3} s for the equilibrium NO concentration in complete combustion, but the required combustion time is 10 times less, i.e. 10^{-4} s. Nevertheless, hydrocarbon flames have sufficiently high NO concentration, as opposed to H_2 and CO flames in the combustion zone (Flagan 1988). C. Fennimore (1972), based on many reactions, suggests that the rapid NO formation scheme is caused due to the binding of nitrogen radical molecules with CH and C_2 in reactions with low energy barriers. Many scientists (Saheed 2016, Ben Rejeb 2017, Choong-Kil 2011, Boukhalfa 2016, Smeringai 2014, Jeffrey 2013) have conducted experiments and corresponding measurements in this area and it can be said that the rapid nitrogen oxide formation scheme in the flame front is a phenomenon that is organically linked to the properties of the hydrocarbon and carbon fuel flames (Klippenstein 2011, Salokyová 2016, Kristensen 1996). Targeted NOx reduction is not yet fully resolved. The rapid oxidation of nitrogen in the flame front is a reliable and well-known fact (Van Oijen 2016, Yu 2016, Fischer 2016, Panda 2014).

Known characteristics of rapid nitrogen oxidation in flames are: a) short process duration, resulting in the formation of a NO (nitrogen monoxide) zone that is located in a small space around the laminar flame front; b) combustion temperature; c) strong dependence on fuel/air input ratio (Zajac 2004, Wunning 1997).

The basic prerequisite for the formation of NOx as combustion products is the natural presence of atmospheric nitrogen, which is an integral part of the combustion air, or presence of fuel nitrogen, which occurs mainly in liquid and solid fuels. For this reason, the theory distinguishes between thermal nitrogen oxides and fuel nitrogen oxides (Myles 2015).

The basic factors influencing the formation of nitrogen oxides in the combustion process are these: a) flame temperature, b) flame geometry, c) partial pressure of oxygen, d) time of combustion mixture presence at NOx formation.

1.2 Methods of NOx reduction in natural gas combustion

Currently used methods of reducing nitrogen oxides released into the atmosphere from combustion processes are divided into primary and secondary methods. The application of primary methods is based on the reduction of nitrogen oxides formation by Govert S. (2015), and Hua P. (2016), in the combustion process itself.

Based on the knowledge of the causes of nitrogen oxide formation, several methods have been developed to eliminate them, of which the most important are: a) reduction of combustion air temperature, b) substoichiometric combustion, c) flue gas recirculation, d) cascade combustion, e) adjustment of oxygen partial pressure, f) reburning (Westbrook 2005, Bowman 1992, Boxiong 2004).

The above-mentioned articles (Varga 2015) have shown that the course of combustion temperatures in a real plant points to a critical zone of the heat field with temperatures above 1775 K. The results show that the nitrogen oxide growth zone corresponds to these temperature ranges (Young 2012, Adams 2016, Jablonský 2015, Terpák 2007). In a case when several burners are installed in the same combustion chamber, the interaction between them may occur (flames interact), thereby significantly increasing the high-temperature zone and exponentially increasing NOx formation.

Taking into account the temperature as the decisive factor for the formation of NOx, it is also necessary to consider the residence time of the flue gas in the combustion chamber of the boiler, in particular, the residence time of the combustion medium in the high-temperature zone. The effective factor that affects both the flame temperature and the residence time is the flame geometry. By adjusting the flame geometry, it is possible to reduce the area of exponential increase in the formation of nitrogen oxides, to reduce the time during which the combustion mixture remains in the high-temperature zone residence time, and to to minimize areas with temperature above 1775 K. It is obvious that when the flame length is reduced, the flame is expanding or, conversely, when it becomes narrower, its length increases. Shortening of the flame length has a positive effect on the residence time of the mixture in the high-temperature zone.

Another reduction method is combustion with low excess air, which has several advantages. Reduction of combustion air volume is made by the control before the burner. In this way, the oxygen partial pressure is reduced. However, it is important to note that in applying this method it is necessary to have flue gas control devices to avoid a drastic drop in oxygen in the combustion mixture, which would lead to over-limit CO formation. The disadvantage of this method is that simply reducing the volume of combustion air in the power industry burners will cause reduction of the swirling effect, as well as the fuel/air mixing. At the same time as the amount of combustion air decreases, the risk of flame instability increases, there is also a risk of increasing the formation of carbon monoxide and soot.

Cascade combustion is a cascade supply of combustion air or fuel to the burner that is used mainly in low emission burners, so-called LNB burners (Low NOx Burners) or cascade fuel feed and cascade air intake into the combustion chamber – system "over fire air" (OFA) (Dunn-Rankin 2008, Gavlas 2013). Cascade combustion technology not only reduces the amount of thermal NOx but also fuel NOx, as fuel and air can be more thoroughly mixed.

There is another way to reduce nitrogen oxides – injecting water into the combustion air supply. The use of this method is particularly suitable for burners (not LNB technologies) that use preheated combustion air (Trisjono 2016). Injecting water into the combustion air results in the catalytic decomposition of H_2O to hydrogen and atomic oxygen in the zones with high flame temperature. The oxygen reacts primarily with carbon, and the reaction produces carbon monoxide. Two hydrogen molecules from the original H_2O bond are able to reduce nitric oxide$\rightarrow N2 + 2H_2O$, thereby reducing NO content. The principle of this method is that atomic oxygen reacts primarily with carbon and not with nitrogen. The disadvantage of this method is the fact that chemically treated water must be available. Another disadvantage is the greater susceptibility to corrosion in the combustion part of the boiler, particularly in areas with insufficient air or flue gas circulation.

2. Materials and Methods

The aim of the research was to assess the effectiveness of particular primary deNOx methods and to find their optimal settings for real boiler operation under limiting combustion conditions. Also, the importance of the interaction of particular deNOx methods and their influence on the overall efficiency of NOx removal in the flue gas, as well as the efficiency of the boiler have been verified. The subject of the research was the heat production unit with four burners installed in the common combustion chamber, as shown in Figure 2. The criterion for comparing the efficiency of NOx reduction in combustion processes is the final concentration of nitrogen oxides in the flue gas under normal conditions.

2.1 Real Device Description

The NOx reduction under limiting combustion conditions using combined primary deNOx methods (CPdeNOx) were tested on a simulation model created in ANSYS Fluent, and simultaneously on a real device - Steam Membrane Boiler OK 60 ČKD Dukla (Figure 1).

There are 4 identical industrial burners installed in the boiler front wall. The burners can operate on natural gas (NG) or heavy fuel oil. In normal operation, natural gas is used as a fuel. Burners belong to low NOx type. The maximum content of nitrogen oxides, according to the manufacturer's technical documentation, per burner should not exceed 100 mg/m^3, provided that it is operated under normal conditions and operating on NG in full range.
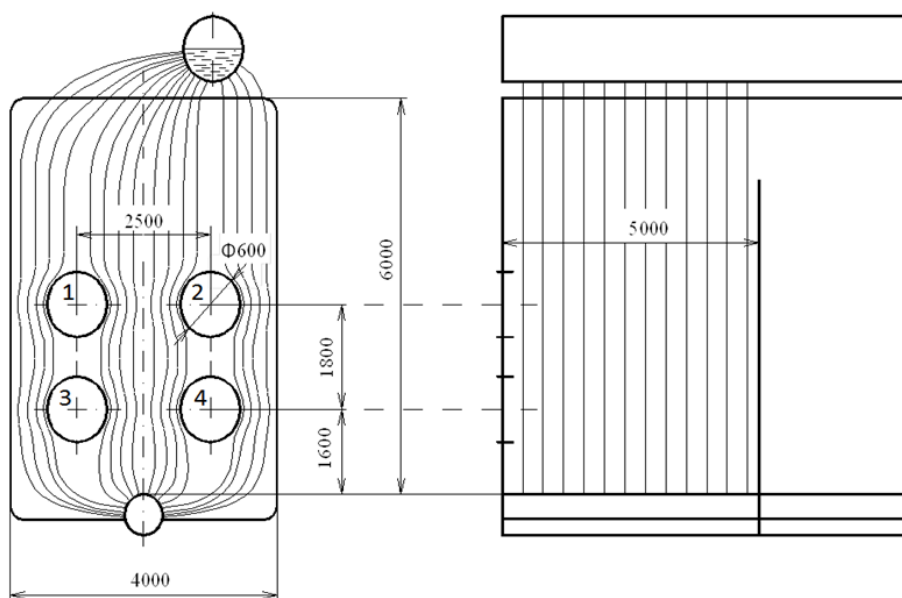

Figure 1. Scheme of boiler OK 60 ČKD Dukla.

The basic technical parameters of the boiler and burners are given in Table 1.

Table 1. Technical parameters of the boiler and burners.

Boiler type	OK 60 ČKD Dukla
Manufacturer	ČKD Tatra Kolín
Highest overpressure	4.5 MPa
Nominal overpressure	3.8 MPa
Designed overpressure	4.0 MPa
Hearth type	overpressure
Nominal steam output	60 t.h^{-1}
Efficiency at nominal parameters	90%
Fuel	NG/HFO
Minimum output	30 t.h^{-1}
Nominal steam temperature	720 K
Nominal feed water temperature	420 K
Burner type	VKH-17.8-1P
Manufacturer	PBS Třebíč a.s.
Nominal thermal output	17.8 MW
Gaseous fuel NG consumption	1 800 m^3.h^{-1}
Nominal pressure of gaseous fuel – NG	50 kPa
Liquid fuel HHO consumption	1.6 t.h^{-1}
Nominal pressure of liquid HHO fuel	3.2 MPa
Number of air fans	2
Output of air fans	2 x 12 m^3.s^{-1}
Output of smoke fan	37.6 m^3.s^{-1}
Designed under pressure in the hearth	20 Pa
Combustion air temperature	475 K
Number of burners	4
Burner type	VKH 17.8 1P
Burner manufacturer	PBS Třebíč
Max burner output	18 000 kW
Gaseous fuel consumption	1 820 Nm^3.h^{-1}
Burner regulating range at gaseous fuel	1:5
Gas overpressure before the burner	100 kPa
Combustion air pressure	1 600 Pa
Max. concentration of NOx (NG/HFO)	100/450 mg.m^{-3}
Max. concentration of CO (NG/HFO)	50/80 mg.m^{-3}

2.2 Description of the Measuring Device

Measurements of gaseous pollutant concentrations of CO, NOx, SO_2, CO_2 as well as O_2 were performed using the HORIBA ENDA 680P emission measurement system. The principles of measuring NOx, SO_2, CO_2, CO are based on modulated non-dispersive infrared detection in the gas flow cross section, and O_2 measurement is performed by magneto-pneumatic detection. The continuous measurement of the observed variables was performed on the basis of physical measurement principles and was evaluated as the average of half-hour values of mass concentrations. The measurement chain diagram is shown in Figure 2.
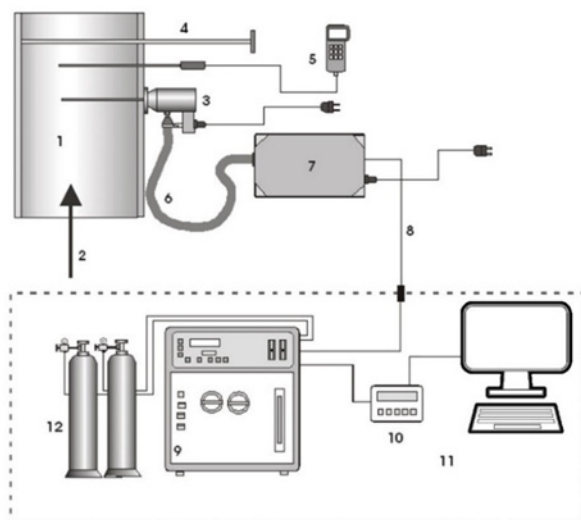
Figure 2. Measuring scheme: 1 – flue gas pipe, 2 – flue gas flow direction, 3 – probe with heated filter for solids, 4 – calibrated rod for measuring pipe dimensions, 5 – thermometer, 6 – heated sampling hose (up to 200°C), 7 – pre-treatment unit with sample cooler and water vapour separator, 8 – Teflon hose (unheated route of treated sample), 9 – HORIBA ENDA 680P multicomponent analyser with 2nd grade sample treatment and vacuum pump, 10 – data logger, 11 – PC, 12 – calibration gases.

The location of the sensor of HORIBA ENDA 680P analyzer, the burners and the boiler OK 60 ČKD Dukla are shown in Figure 3. The probes of the measuring device were placed in the upper part of the boiler flue duct.

Figure 3. Boiler OK 60 ČKD Dukla. Clockwise: one of 4 gas burners; the top of the boiler duct; height view of the boiler; label with technical parameters of the boiler.

2.3 Description of the Experiment

The main idea of the experiment was to determine the boiler efficiency and to compare all primary deNOx methods suitable for implementation on a given boiler type.

The following primary denitrification methods were selected for processing the experiment:
- Adjustment of oxygen partial pressure
- Cascade combustion
- Injection of auxiliary substances
- Circulation

Each of the methods was tested separately, to determine its effectiveness in the combustion process in terms of nitrogen oxides formation. The whole experiment was divided into four stages.

The first stage is the creation of an accurate simulation model of the membrane boiler OK 60 ČKD Dukla with four burners VKH-17.8-1P using the ANSYS software tool.

The main objective of the first stage is to create an accurate model of the combustion plant with the following validation of the simulation results. Within this validation, the real measurements were performed on the device under different conditions.

The second stage includes the implementation and testing of the primary deNOx methods using the simulation model. The effect of the implementation of each method was evaluated separately by comparing the simulation results with appropriate reference simulation.

In the third stage, the interaction effect of the combination of primary deNOx methods and their impact on NOx formation and overall boiler performance was monitored and evaluated using the simulation environment. Also, the measures have been proposed and simulated to reduce nitrogen oxides in the real plant.

The aim of the last stage was to confirm/validate the results of stage 3 using a series of measurements that were performed in the semi-operational mode.

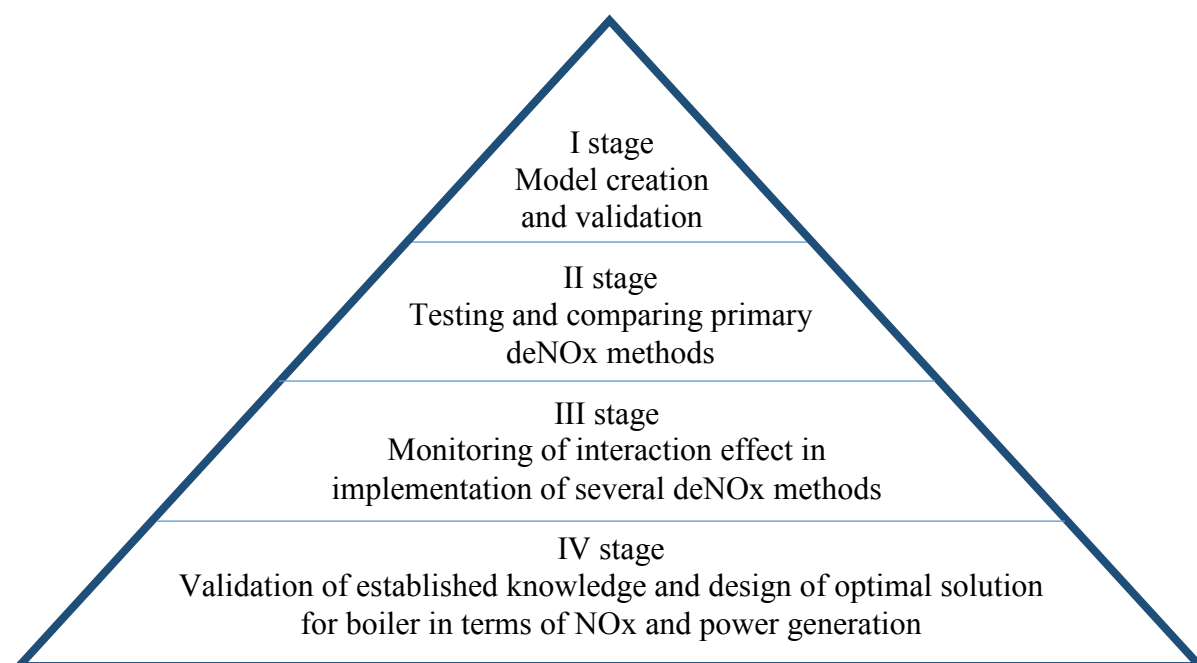The diagram of the experiment is shown in Figure 4.

Figure 4. Diagram of the experiment.

3 Experiment

The main idea of the experiment was to determine the efficiency and compare all the primary deNOx methods, which are suitable for implementation on the given type of boiler.

3.1 Modelling

In order to compare the effectiveness of each deNOx method, a computer model was developed. Non-premixed combustion was solved using the ANSYS Fluent simulation software. The CAD models of the boiler and burners were created in ANSYS Design Modeller according to the technical documentation.

As a part of a model, the network has been created for Computational Fluid Dynamics (CFD) Fluent Solver with Proximity, and Curvature Advanced Size functions. Due to the difference in input and output dimensions, the minimum size of the element side was proposed 1.455 mm according to Proximity function, and the maximum size was 500 mm. The element growth rate parameter was set to the value of 1.35. In accordance with these settings, 60% of all elements had an orthogonal quality of more than 0.76, and the lowest value was 0.13, with less than 1% of the elements. According to the skewness statistic, 80% of the elements had the quality of 0.38, with less than 1% of the elements belonging to the worst quality group of 0.7-0.97. The total number of simulation model elements was 18,923,062.

When defining the turbulence model, verification simulations were implemented using integrated modules RANS and then LES. The results of the boiler simulations showed that from the point of view of the calculation stability, the realizable k-epsilon model, which was also applied for the simulations, was the best.

The solved transport equation for the realizable k-epsilon model has the following form:

$$\frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_j}(\rho k u_j) = \frac{\partial}{\partial x_j}\left[\left(\mu + \frac{\mu_t}{\sigma_k}\right)\frac{\partial k}{\partial x_j}\right] + G_k + G_b - \rho\varepsilon - Y_M + S_k \tag{1}$$

and

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \frac{\partial}{\partial x_j}(\rho\varepsilon u_j) = \frac{\partial}{\partial x_j}\left[\left(\mu + \frac{\mu_t}{\sigma_\varepsilon}\right)\frac{\partial\varepsilon}{\partial x_j}\right] + \rho C_1 S_\varepsilon - \rho C_2 \frac{\varepsilon^2}{k+\sqrt{\varepsilon v}} + C_{1\varepsilon}\frac{\varepsilon}{k}C_{3\varepsilon}G_b + S_\varepsilon \tag{2}$$

where

$$C_1 = max\left[0.43, \frac{\eta}{\eta+5}\right], \eta = S\frac{k}{\varepsilon}, S = \sqrt{2S_{ij}S_{ij}} \tag{3}$$

- In these equations, G_k represents the generation of the kinetic energy of turbulence due to mean velocity gradients.
- G_b is the generation of kinetic energy by turbulence considering buoyancy.
- YM represents a manifestation of fluctuating dilation in compressible turbulence to the overall scattering rate.
- $C_{1\varepsilon}$, $C_{3\varepsilon}$, and C_2 are constants.
- σ_k and σ_ε are turbulent Prandtl numbers for *k* and *e*.
- S_k and S_ε are user-defined source formulas.

The formula for normal Reynolds stress of incompressible average flow results from the combination of Boussinesq approximation and the definition of eddy viscosity.

$$\overline{u^2} = \frac{2}{3}k - 2v_t\frac{\partial U}{\partial x} \tag{4}$$

Eddy viscosity is calculated as:

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon} \tag{5}$$

In the case of the realizable k-epsilon model, Cµ is not a constant value:

$$C_\mu = f(k, \varepsilon, \Omega, \omega) \tag{6}$$

Where
Ω – rotation speed tensor,
ω – angular velocity.

The PDF model for non-premixed combustion had additional settings: equilibrium state relation, non-adiabatic energy treatment with 102 325 Pa combustion chamber operating pressure, number of mean mixture fraction points 40, the maximum number of components 30, number of enthalpy points 45.

The PDF compositions, like Laminar Finite-Rate and model, should be used to simulate chemical kinetic effects with a finite extent in turbulent reaction flows. With a suitable chemical mechanism, kinetically controlled elements such as CO and NOx, as well as flame extinction and ignition can be predicted (Boukhalfa 2016).

The transport equation PDF is derived from the Navier-Stokes equation as (Smeringai 2014):

$$\frac{\partial}{\partial t}(\rho P) + \frac{\partial}{\partial x_i}(\rho u_i P) + \frac{\partial}{\partial\psi_i}(\rho S_k P) = -\frac{\partial}{\partial x_i}\left[\rho\langle u_i''|\psi\rangle P\right] + \frac{\partial}{\partial\psi_i}\left[\rho\left\langle\frac{1}{\rho}\frac{\partial J_{i,k}}{\partial x_i}\Big|\psi\right\rangle P\right] \tag{7}$$

Where
P – common composition of PDF and Favre,
ρ – average liquid density,
u_i – Favre velocity vector,
S_k – the rate of reaction of *k* elements,
ψ – space composition vector,
u_i'' – vector of fluid velocity fluctuation,
J_{ik} – molecular diffusion flow vector.

Notation $\langle \ldots \rangle$ indicates expectations, and $\langle A \mid B \rangle$ is the conditional probability of event A when event B occurs. The turbulent scalar flow is not closed and is modelled by the assumption of diffusion gradient transition (Song 2012):

$$-\frac{\partial}{\partial x_i}\left[\rho\langle u_i^{''}|\psi\rangle P\right] = \frac{\partial}{\partial x_i}\left(\frac{\rho\mu_t}{Sc_t}\frac{\partial P}{\partial x_i}\right) \qquad (8)$$

Where
μ_t is turbulent viscosity,
S_{ct} is Schmidt number.

The Turbulence model specifies µt for the composition of PDF simulation.

For all flows, ANSYS Fluent solves the mass and momentum conservation equations. For flows that include heat transfer or compressibility, another energy conservation equation is solved. For flows involving mixing or reactions of the components, the component conservation equation is solved or, if the model is applied for non-premixed combustion, the conservation equations for the mixture fraction and its dispersion are solved. In the case of turbulent flow, additional transport equations are solved.

For the external surfaces of the model, boundary conditions of the second kind were selected. The heat dissipated through the boiler peripheral wall was calculated using a separate model, the determined value is 0.57 MW.

To reduce the computational time, a steady model of combustion and turbulence was chosen. The time processes were chosen as less important because the stationary calculation shows the most likely variation of the combustion processes, as well as the most likely processes of the regular boiler operation mode.

The velocity specification for air and gas inputs has been proposed as a value perpendicular to input with an absolute reference value; the turbulence specification was determined according to the intensity and hydraulic diameter.

Figure 5 shows the CAD model of the burner. The geometry of the combustion chamber and part of the flue gas duct was optimized in terms of calculation time without significant influence on the calculation accuracy.
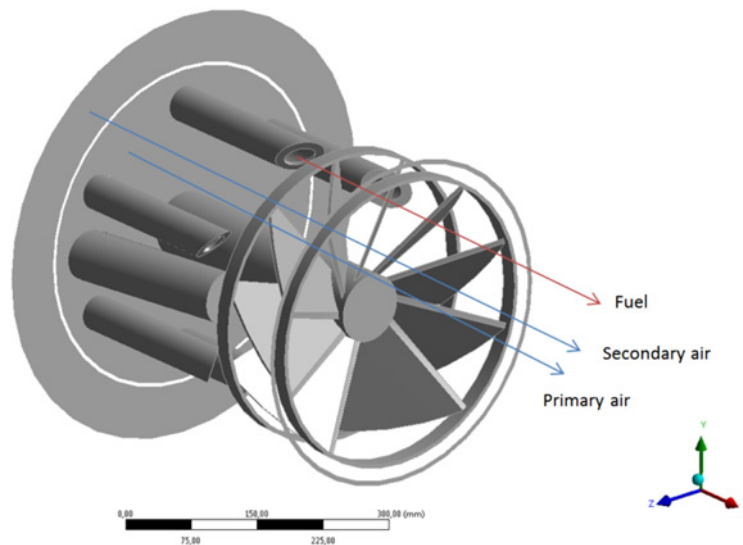

Figure 5. The CAD model of the burner.

3.2 Model Simulation

The geometry of the simulation model was drawn precisely according to the technical parameters and dimensions of the burners and the boiler combustion chamber (Fig. 2 and Table 1), as well as the distances between the burners in the horizontal and vertical planes. The combustion simulation parameters were determined from the burner performance ratios and the corresponding amount of natural gas consumed as the fuel and combustion air as the oxidant. The average composition of the natural gas used in the simulation model (Table 2) was determined from the values representing the volume ratios of the individual components in the real operating conditions of the boiler.

Table 2. Composition of natural gas.

Composition of natural gas [mol %]							
Methane	Ethane	Propane	Butane	Pentane	Hexane +other	Carbon dioxide	Nitrogen
95.361	2.5231	0.6437	0.8504	0.0407	0.0255	0.2351	0.3205

The model validation was done by comparing the simulation output parameters with the real measured values and the calculated values. All monitored parameters of the simulation can be divided into three basic groups:

• Basic physical parameters such as temperature, velocity, pressure, density, viscosity, turbulence energy, heat and mass flows;

• Input parameters: gas and air composition, the content of fuel and air partial elements;

• Output parameters: the content of CO, CO_2, O_2, N_2, NO, NO_2, N_2O, H_2O and other flue gas components.

A series of simulations (j) were performed with increasing iteration number (j * 10E3). The results of which are shown in Table 3. With respect to the measurement method, the concentration values were determined as the mean values at the output of the simulation model.

Table 3. Simulation results.

Exp.	Max. temperature [K]	Min. temperature [K]	NO [mg/m^3]	NO$_2$ [mg/m^3]	N$_2$O [mg/m^3]	The volume of high temperature, [m^3]	Number of iterations
1	2155.5	287	347,2	16.32	0.00088	24	1000
2	2156.2	287	347,8	16.45	0.00091	24	2000
3	2156.1	287	348,1	16.67	0.00094	24	3000
4	2156.2	287	348,3	16.68	0.00096	24	4000
5	2156.3	287	348,5	17.14	0.00097	25	5000
6	2156.6	287	348,6	17.18	0.00098	25	6000
7	2156.8	287	348,9	17.21	0.0010	25	7000
8	2157	287	349,1	17.22	0.0010	25	8000
9	2157.1	287	349,1	17.23	0.0011	25	9000
10	2157.1	287	349,2	17.23	0.0011	25	10000

The graphical visualization of the combustion chamber interior displays processes taking place in the boiler. Figures 6 and 7 show the simulation characteristics. The temperature field patterns are shown in Figure 6, and the NO concentrations and kinetic energy are shown in Figure 7 in the horizontal and vertical plane inside the combustion chamber.
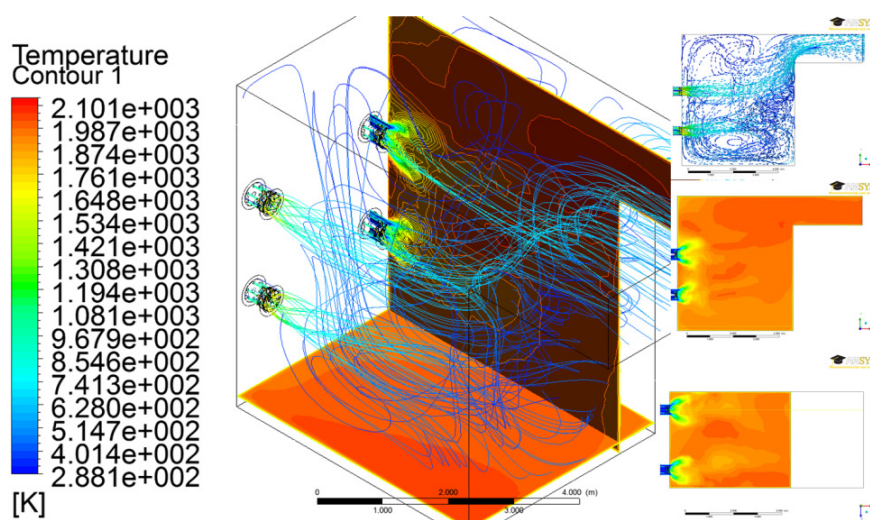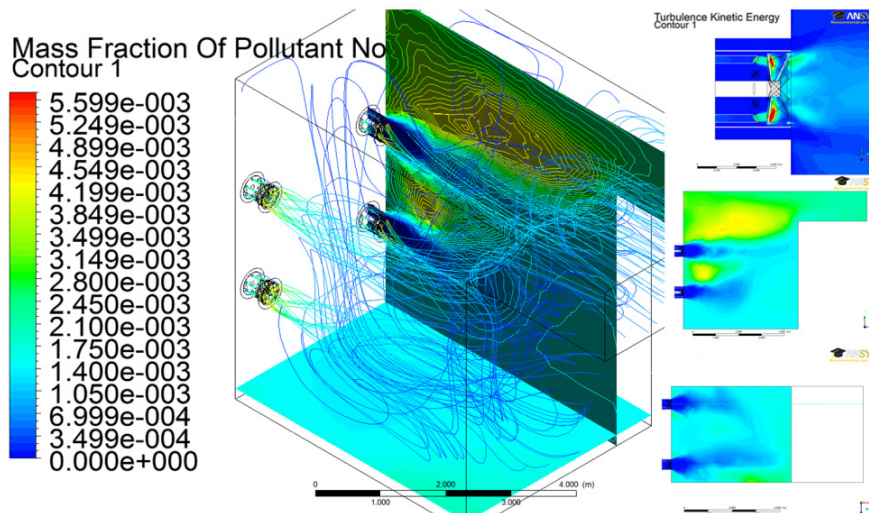

Figure 6. Temperature field patterns.

Figure 7. The NO concentrations and kinetic energy patterns.

For the analysis of the mechanism, as well as for the determination of the worst spot for the formation of nitrogen oxides in the boiler, the diagrams of NOx content were created along the horizontal axis of each of the 4 burners, as well as along the horizontal axis of the boiler in the area between the burners.

Figure 8 shows the distribution of the NO mass fraction in dependence on the horizontal distance from the burner and from the horizontal axis of the boiler.
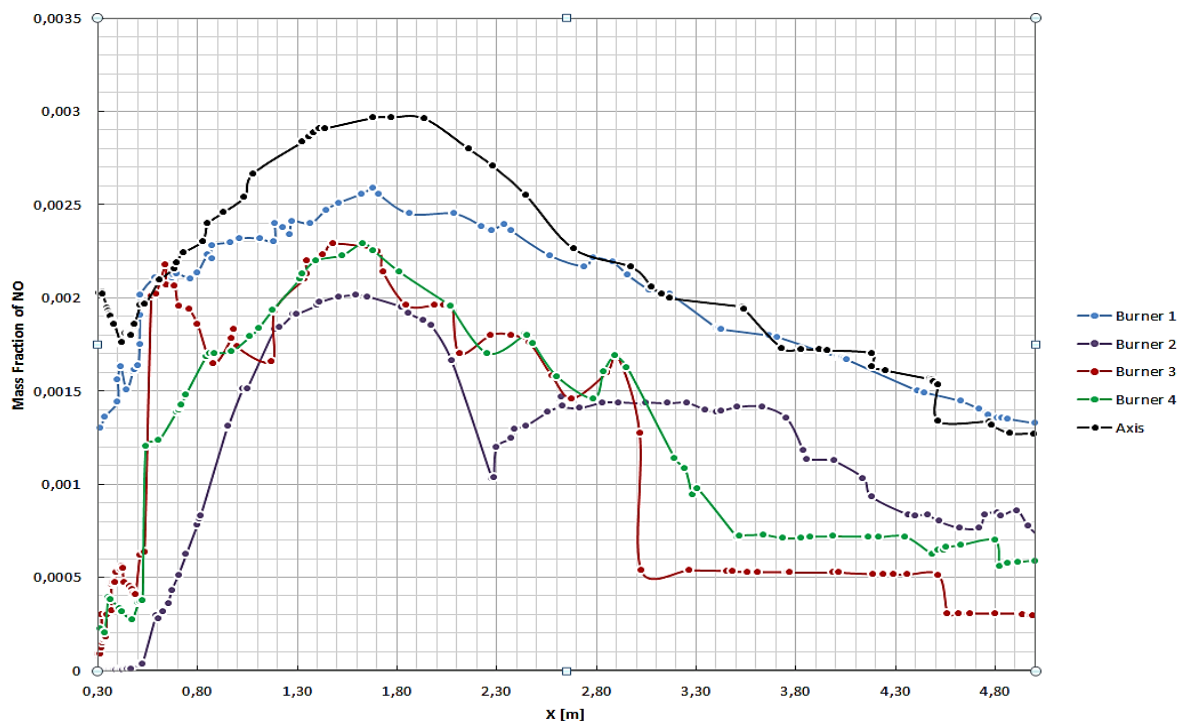

Figure 8. The distribution of the NO mass fraction in dependence on the horizontal distance from the burner and from the horizontal axis of the boiler.

3.3 Model Validation

With regard to the list of standard controlled values and the possibilities of the measuring technique, the flue gas temperatures, oxygen content, carbon dioxide content, as well as the mass concentration of nitrogen oxides in the flue gas were compared.

Table 4 lists the measured values as the mean half-hour values of volumetric and mass concentrations of pollutants calculated for normal pressure, temperature, and the oxygen reference value of 3% at full boiler load.

Table 4. Real measurement results.

Measurement time [h:min]	8:45-9:15	9:15-9:45	9:45-10:15	10:15-10:45	10:45-11:15	Value	
						max	mean
Content [% vol.]							
O_2	7,27	7,15	7,08	6,87	6,85	7,27	7,04
CO_2	7,34	7,41	7,44	7,53	7,53	7,53	7,45
Mass concentration [mg.m^{-3}]							
NO_x	351	353	353	344	348	353	350
CO	3	2	2	6	3	6	3

When comparing simulation model output data with real data, the model was classified as appropriate, including its boundary conditions, the number of repetitions, selected calculation modules, etc. From the comparison of the simulation model results (Table 3) and the measured values (Table 4) of the mass concentrations calculated for reference conditions (normal temperature T_n = 293.15 K, normal pressure p_n = 101,325 Pa) it can be seen that the simulation model shows high compliance level of parameters, especially temperatures, also O_2, CO, CO_2, and NOx concentrations.

It can be seen in Figures 4 and 5 that the dimensions of the combustion chamber and the axial distances between the boiler burners can cause the formation of limiting conditions. These conditions are characterized by the extreme heat load of the combustion chamber Q_n = 0.59 MWm^{-3}. The graphical visualization of the interior of the combustion chamber shows that the burner flames have a direct impact on the back wall of the combustion chamber and confirm the theoretical assumptions regarding the combustion under the limiting conditions formulated in the previous section. Simulations have also confirmed that, because of the short distance between the burners, the high-temperature area increases due to the interaction of the flames, especially when the boiler operates at maximum power.

4 The Results

4.1 Simulation Results

In order to determine the effectiveness of separate primary deNOx methods, a series of simulations were performed in ANSYS Fluent.

4.1.1 Oxygen Partial Pressure

One of the important parameters in terms of combustion stoichiometry, as well as flow and mixing dynamics, is the ratio of combustion air and fuel. From the literature (Varga) it is known that by setting the correct combustion air/fuel ratio, nitrogen oxides production can be reduced by 10 to 15%. From the physic-chemical point of view, the optimum amount of air in the combustion of natural gas is within the range of 102 to 107% of the amount required for complete burning (n = 1.02 - 1.07).

Series of simulations was performed varying amounts of combustion air. On the basis of theoretical knowledge, the effect of the combustion air ratio ranging from 90% to 110% of the stoichiometrically required (complete burning) amount was tested. Based on the results of the simulations, the characteristic diagram (Figure 9) was created.
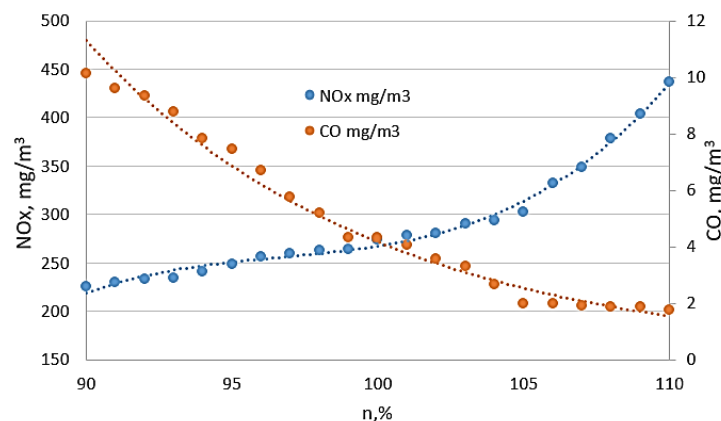

Figure 9. Characteristic diagram of the effect of combustion air ratio ranging from 90% to 110%.

Based on the results of the simulation, it can be concluded that from the viewpoint of the stoichiometry of combustion and NOx formation, the optimal combustion is at 105% from stoichiometrically needed air. At the given value of *n* it is possible to use the fuel efficiently and also, in view of the NOx curve, there is no rapid NOx increase due to higher temperatures in the combustion chamber, and there is no increase of oxygen amount. The graphical visualization of the processes in the combustion chamber is shown in Figure 10.
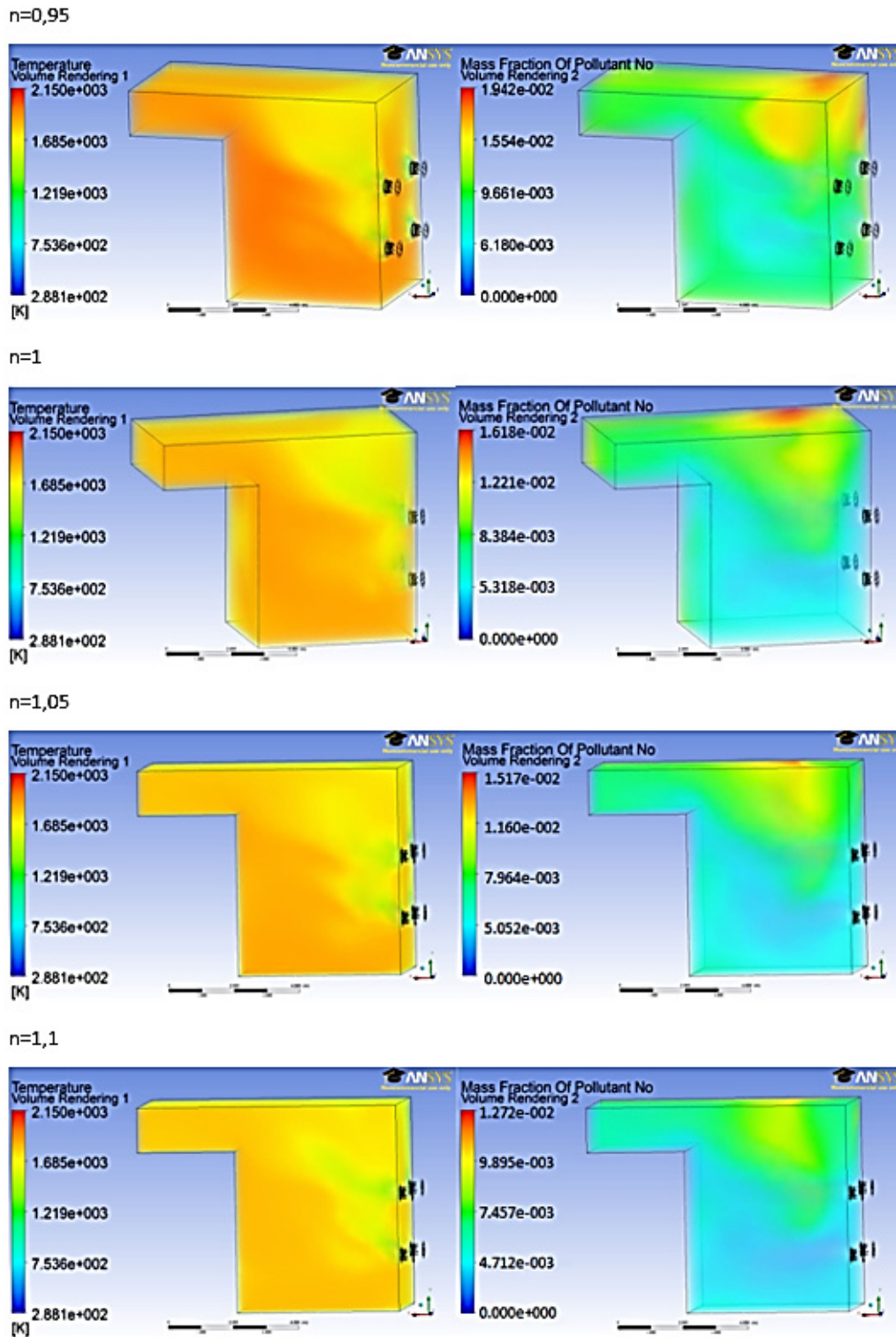

Figure 10. Graphical visualization of processes in the boiler combustion chamber, at different O_2 partial pressures.

In comparison with the validation model, it is evident that the NOx content decreased by 12.5% to about 305 mg/m^3. This decrease is mainly due to the reduction of the oxygen partial pressure, resulting in a decrease of high-temperature range, and hence in the decrease of the thermal NOx. In this case, the CO content increased

only by 1%, i.e. by 2.2 mg/m^3, and the overall boiler output (calculated on the basis of thermal balance) decreased by 0.5% to 59.5 MW.

4.1.2 Cascade Combustion

Using modern burners with combustion air distribution to the primary and the secondary air (cascade air supply), it is very important to maintain their proper ratio. It has been established (Rimar) that, depending on the shape of the combustion chamber, flame shape and other parameters, the ratio should be in the range of 65-35% to 80-20%. Simulation without cascade air supply has also been proposed to determine efficiency in particular conditions. Table 5 shows the values of primary/secondary air ratios for each simulation.

Table 5. Primary/secondary air ratio for simulations.

Ratio	50:50	65:35	70:30	75:25	80:20
Primary air [m^3/s]	2.5	3.25	3.5	3.75	4
Secondary air [m^3/s]	2.5	1.75	1.5	1.25	1

Simulation with the same primary and secondary air ratio is applied to determine the efficiency of the cascade air supply in the boiler. Figure 11 shows the results of cascade air supply simulations.
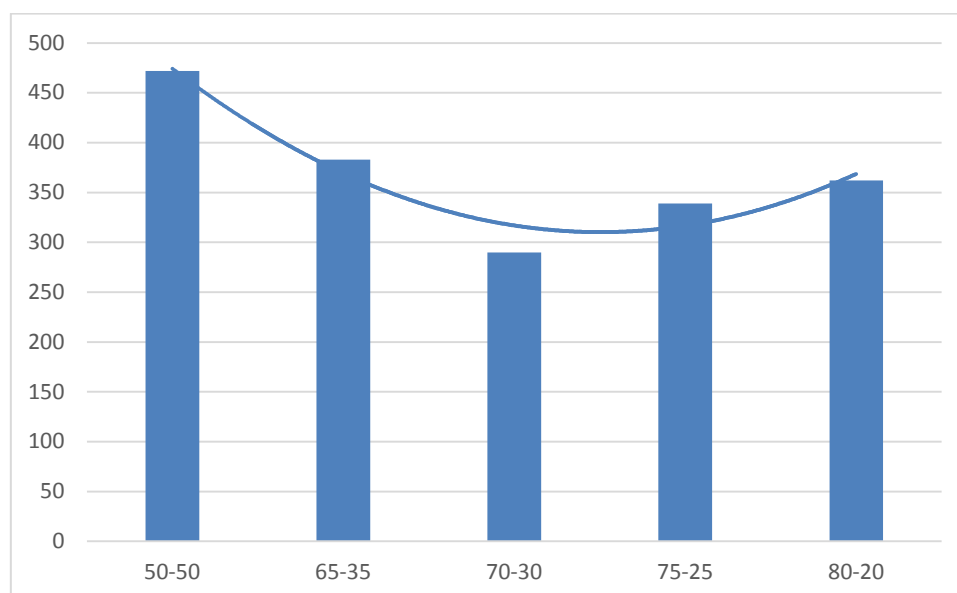

Figure 11. Effect of cascade air supply.

Based on the results of the simulation, it can be stated that the optimum ratio of cascade air supply is 70-30%. When comparing the reference simulation of combustion with a cascade air supply of 70-30%, it was possible to reduce the nitrogen oxides content by 20%, i.e. up to 290 mg/m^3. At the same time, the boiler output did not change. The NOx reduction is associated with lower temperature in the flame centre, and with an increase of the flame length. The graphical visualization of the processes in the combustion chamber is shown in Figure 12.
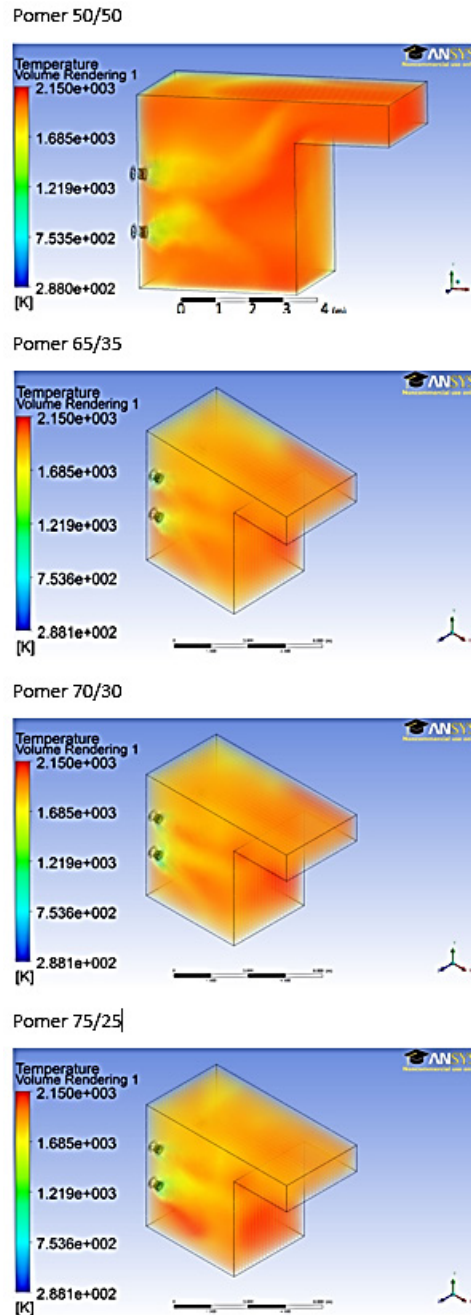
Porner 50/50

Porner 65/35

Porner 70/30

Porner 75/25

Figure 12. Graphical visualization of processes in the boiler combustion chamber, at different combustion air ratios.

4.1.3 Injection of Auxiliary Substances

The analysis of the possibilities of applying the method of auxiliary substances injection in the real device has lead to the following conclusions:

• Reducing the temperature of the combustion air or fuel would lead to a significant drop in boiler performance.

• The addition of reacting agents into the combustion process has been assessed to be very cost-intensive in most boilers because it requires the installation of a whole range of additional equipment.

For these reasons, the method of reducing the flame temperature of the burners by the addition of cooling agents was chosen as appropriate. Water vapour was chosen as the cooling agent at 300 K, due to the type of used equipment and the water vapour availability.

Discrete analysis of the effect of vapour injections was performed to demonstrate NOx reduction efficiency and to test theoretical assumptions in the simulated environment. The injection water vapour volume for impact analysis was applied from 0 kg/h to 120 kg/h with the step of 10 kg/h. The limit value of 120 kg/h was determined as maximum possible on the given type of burner, in order to avoid a significant change of flow and hence the flame dimensions.

Table 6. Outputs of combustion simulation with water vapour injection into primary air of burners.

No.	Water vapour volume [kg/h]	Maximum temperature in boiler [K]	Boiler power ratio [%]	NO [mg/m^3]	N$_2$O [mg/m^3]	High-temperature volume [m^3]
1	0	2157	99.37336	349	0.001	25.3
2	10	2143	98.75864	346	0.001	25
3	20	2131	98.92435	344	0.001	23.7
4	30	2120	98.12938	339	0.001	22.2
5	40	2089	97.40332	335	0.001	20.6
6	50	2064	96.52132	328	0.001	18.3
7	60	2012	95.70154	321	0.0009	16.2
8	70	1971	95.10803	312	0.0009	14.6
9	80	1929	94.33792	305	0.0009	12.9
10	90	1885	93.25225	299	0.0009	10.1
11	95	1839	92.89907	295	0.0008	9
12	100	1818	91.96816	290	0.0008	8.5
13	105	1783	91.28704	288	0.0008	7.9
14	110	1707	89.67808	274	0.0007	4.2
15	120	1643	85.03848	262	0.0006	3.1

It can be seen from the table that the critical point for the given boiler is at 100 kg/h of injected water vapour. On the basis of acquired values, the analysis was carried out for the dependence of NOx amount on water vapour amount, maximum flame temperature, and boiler output (Figure 13).
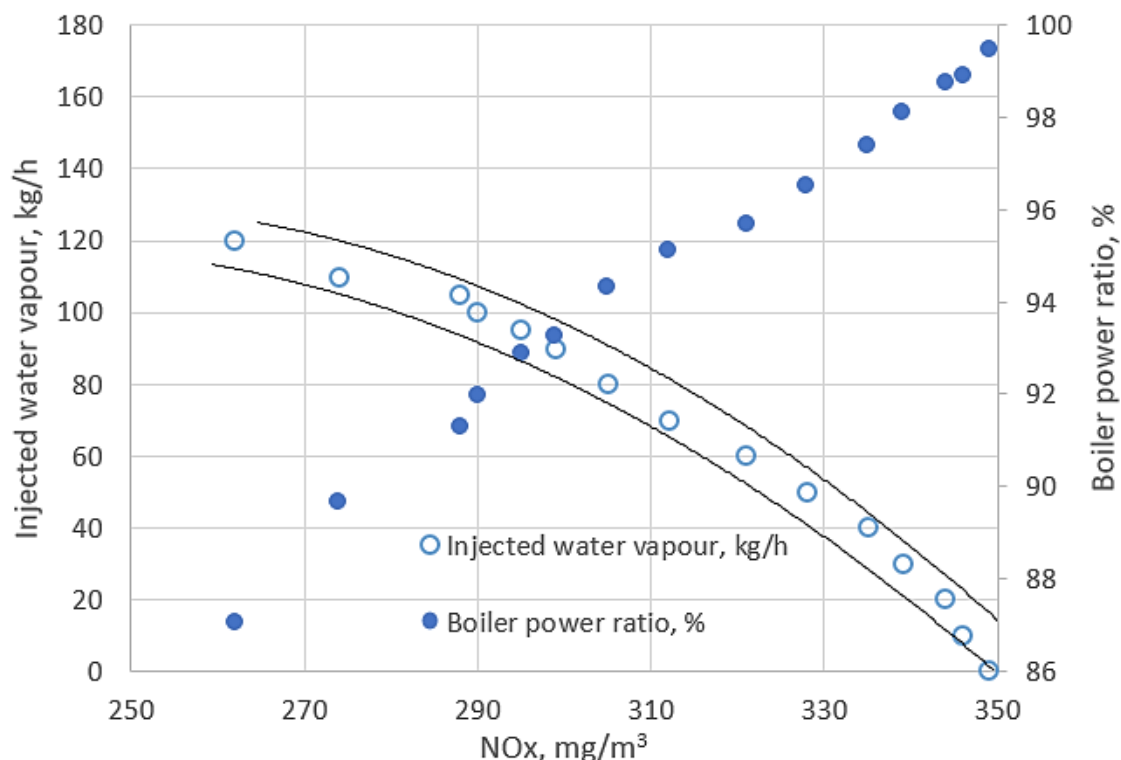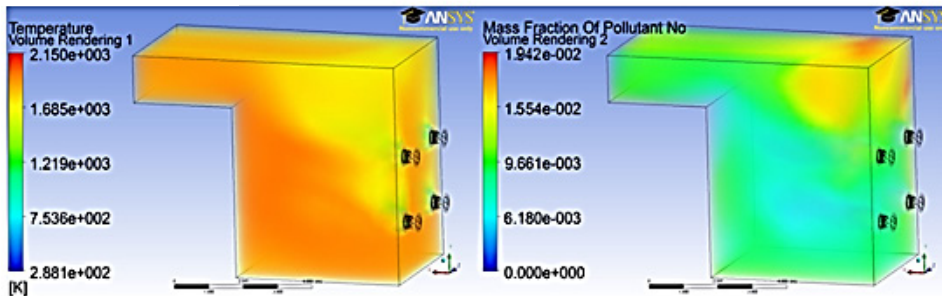

Figure 13. Dependence of water vapour injection and maximum burner flame temperature on nitrogen oxide formation.

The area of overlap of dependence curves of the boiler power ratio and water vapour injection on the NOx formation indicates the optimal level of water vapour injection in terms of boiler performance and nitrogen oxide formation.
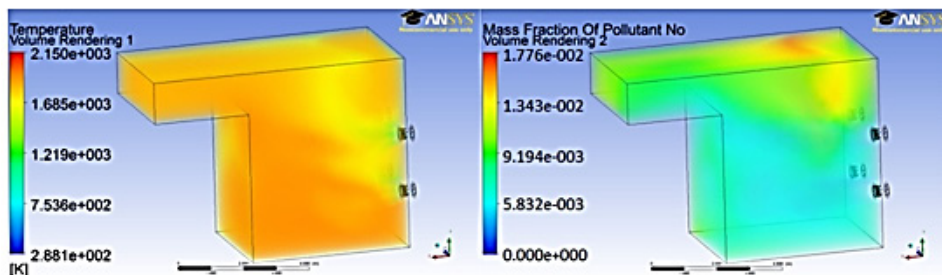
On the one hand, the injection of less than 90 kg/h of water vapour in the boiler results in a small reduction in nitrogen oxides formation but does not substantially affect boiler performance. On the other hand, injection of more than 110 kg h of water vapour has a significant impact on the formation of nitrogen oxides but also has a significant negative impact on boiler performance.

By injecting 120 kg/h of water vapour, the NOx content could be reduced by 25% to approx. 260 mg/m^3 but with such a volume of injected water vapour, there was also a significant reduction of the boiler output by about 15%.
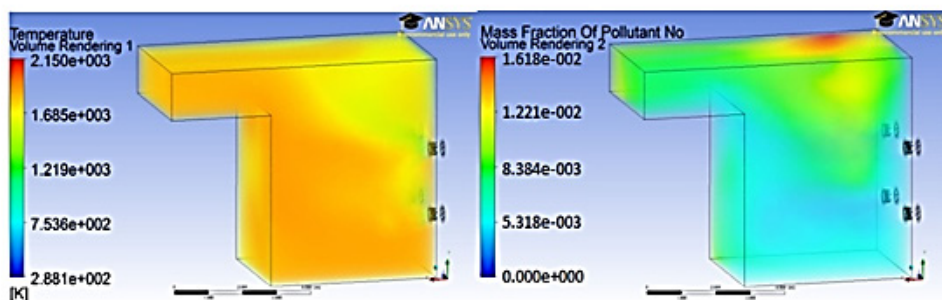
Injection 10kg/h

Injection 50kg/h
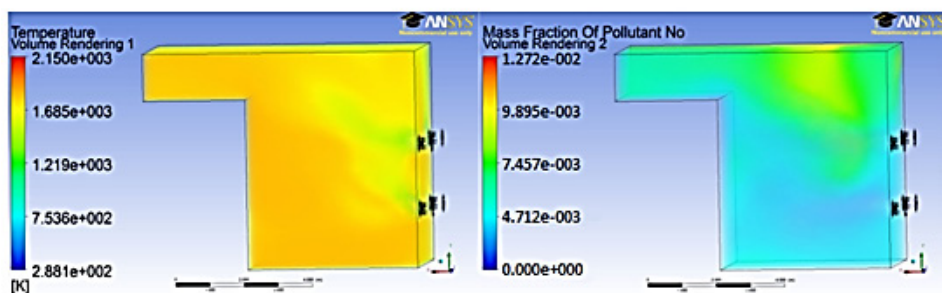
Injection 100kg/h

Injection 120kg/h

Figure 14. Graphical visualization of the processes in the boiler combustion chamber, with different volumes of injected water vapour.

According to the results of the simulations and the theoretical review, the analysis of the effect of water vapour injection at different thermal loads of the combustion chamber is shown in Figure 15.
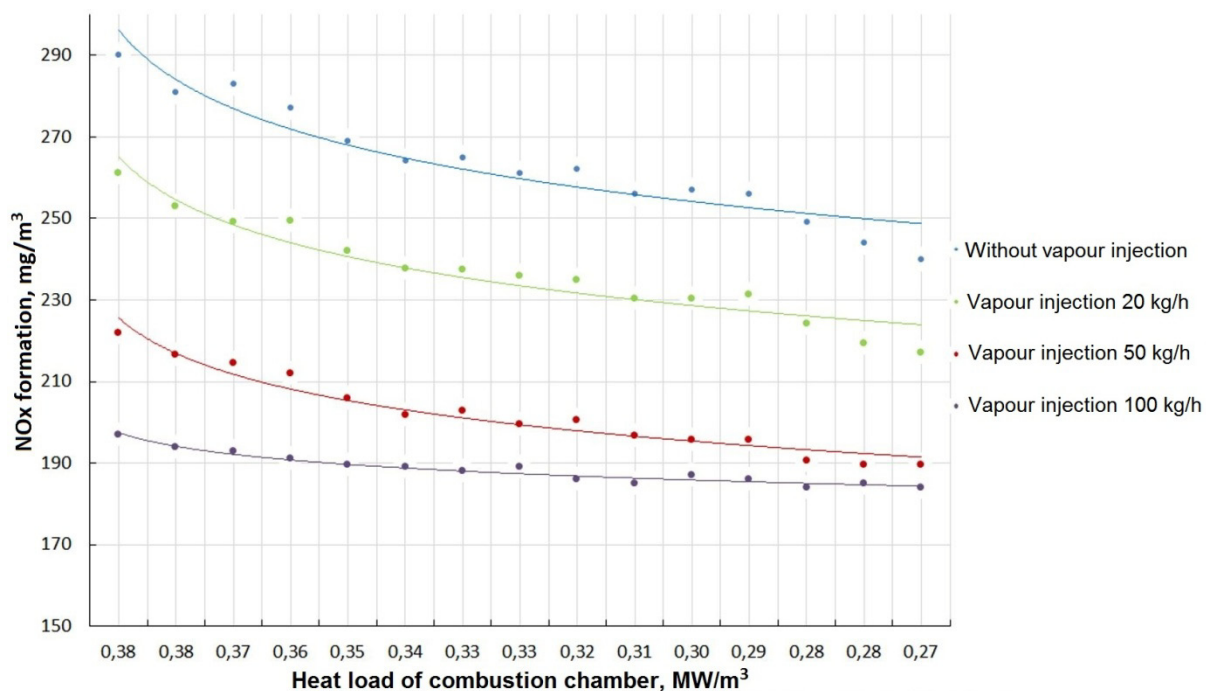
Figure 15. Influence of water vapour injection at different thermal loads of the combustion chamber.

From the results of the simulation, it was found that the decisive parameter in solving the problem of the formation of thermal nitrogen oxides is the thermal load of the boiler combustion chamber. The critical value with respect to the formation of nitrogen oxides was set at 0.33 MW/m^3.

4.1.4 Flue Gas Circulation

The main idea of flue gas circulation is to increase the time which the flue gas retains in the combustion chamber of the boiler. Based on the carried-out analysis, it was determined that one of the essential ways of improving circulation is the boiler design change related to the location of the burners, or to the shape of the combustion chamber.

The mass flow analysis in the combustion chamber has shown that the flames of the upper pair of burners tend to bend upwards due to the influence of the lower pair, and thus about 40% of the flue gases go straight to the exhaust of the combustion chamber. It was proposed to solve this problem by reducing the power of the lower pair of burners by 150 to 300 kW, which is 1% to 2%. The simulation results are shown in Figure 16.
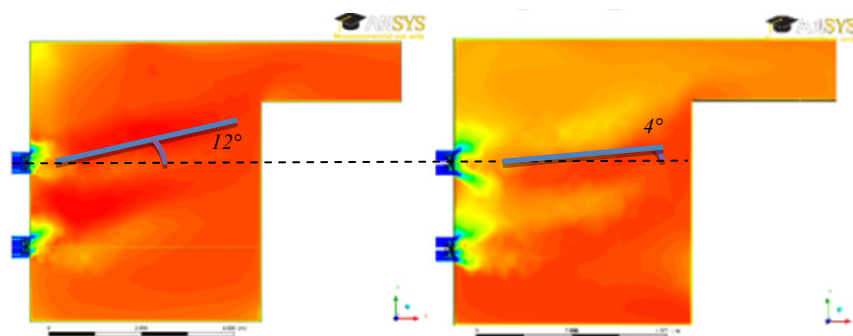

Figure 16. Results of simulations when changing flue gas circulation.

From the figure, it can be seen that decreasing the power of the lower pair of burners by 1% resulted in moving the flames of the upper pair of burners closer to the boiler axis. The improvement in flue gas circulation associated with this effect has resulted in a reduction of NOx content by 2% while reducing performance by only 0.5%. Further reduction of the lower burners performances had the opposite effect in terms of NOx formation, due to the flame interaction.

4.2 Proposal for Burner Setting

On the basis of simulations described in the previous chapters (4.1.1-4.1.4), optimum boiler settings have been proposed in terms of performance and nitrogen oxide formation. The following settings have been selected:

- Excess air coefficient: $n = 1.05$
- Primary to secondary air ratio: 70/30%
- Amount of injected water vapour: 100 kg/h
- Performance of lower burners: 99%

The simulation was carried out to confirm the boiler settings. The results of the simulation are shown in Table 7.

Table 7. Simulation results (settings 1).

Maximum temperature in boiler [K]	Boiler power ratio [%]	NO [mg/m^3]	N$_2$O [mg/m^3]	High-temperature volume [m^3]
1812	90.87336	191	0.001	7.5

From the results of the simulation it is evident, that by the means of the proposed settings, the nitrogen oxide content at the exhaust of the boiler combustion chamber decreased by 45%, while the boiler's relative output decreased by about 9%. This reduction of NOx was mainly due to the significant reduction of the flame temperature and hence the reduction of high-temperature volume where thermal nitrogen oxides are formed. Even though by combining primary deNOx methods, the NOx content could be significantly reduced, the effectiveness of each separate method in combination was reduced. Further analysis has shown that the initially selected optimal settings for NOx reduction are no longer optimal due to their combination. The main problem has arisen in reducing of the oxygen partial pressure in the primary flame burning zone. In this respect, simulation with the modified primary/secondary air ratio of 72/28% was carried out. Table 8 shows the simulation results.

Table 8. Simulation results (settings 2).

Maximum temperature in boiler [K]	Boiler power ratio [%]	NO [mg/m^3]	N$_2$O [mg/m^3]	High-temperature volume [m^3]
1812	90.63691	185	0.001	7.,4

Table 8 shows that, by increasing the primary air ratio, a further NOx reduction of 3% to 185 mg/m^3 was achieved, although this led to an increase of NOx content in the stand-alone simulations.

Based on settings 1 and 2, a series of simulations were carried out to determine the effects of interactions of primary deNOx methods. The simulation results are shown in Figure 17.
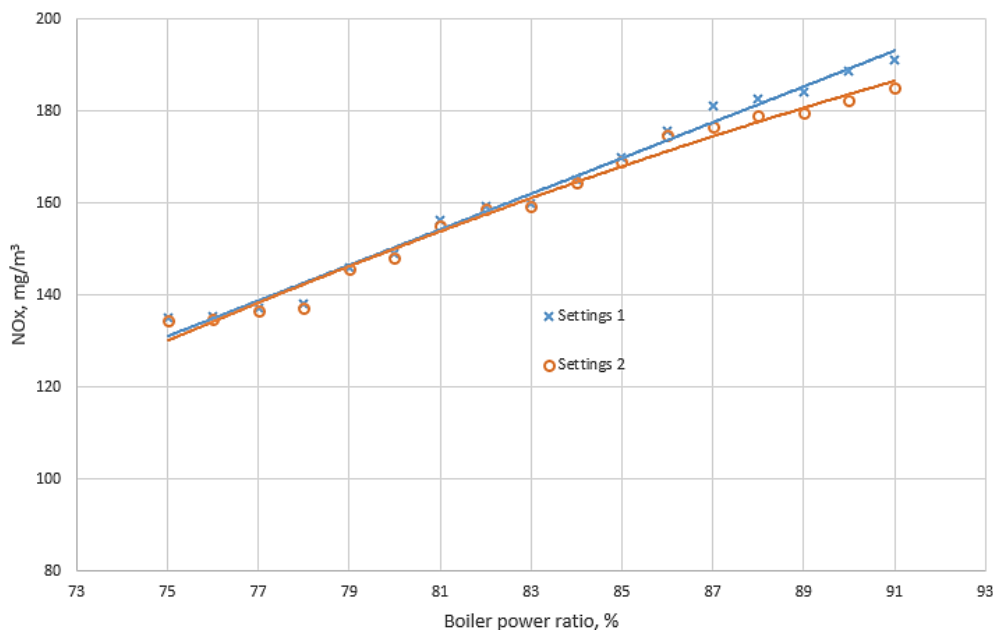

Figure 17. Effects of interaction of primary deNOx methods at different boiler performance.

The curves in the diagram show that the interaction effect is most pronounced at higher boiler output (from 85%). These performances result in a greater thermal load in the combustion chamber, creating a more sensitive environment for the formation of nitrogen oxides. Consequently, combustion plants with the thermal load of the combustion chamber of less than 0.25 MW are less "sensitive", which, in most cases, allows their pattern-setting according to the defined parameters. In contrary, combustion plants with the thermal load of the combustion chamber greater than 0.25 MW require individual approach and accurate operation parameters setting.

4.3 Measurement Results for Proposed Boiler Settings

Based on the selected optimal settings, a series of measurements were made to validate the results of both groups of settings. The measurement results are shown in Table 9 and 10.

Table 9. NOx concentration measurement results for the first settings.

Measurement time [h:min]	8:45-9:15	9:15-9:45	9:45-10:15	10:15-10:45	10:45-11:15	Value	
						max	mean
Contents [% vol.]							
O_2	7.31	7.23	7.22	7.75	6.88	7.75	7.28
CO_2	7.32	7.42	7.38	7.48	7.54	7.54	7.43
Mass concentration [mg.m^{-3}]							
NO_x	198	196	196	187	191	198	193
CO	3	6	2	2	3	6	3

Table 10. NOx concentration measurement results for the second settings.

Measurement time [h:min]	14:00-14:30	14:30-15:00	15:00-15:30	15:30-16:00	16:00-16:30	Value	
						max	mean
Contents [% obj.]							
O_2	7.34	7.32	7.33	7.22	7.33	7.34	7.31
CO_2	7.26	7.30	7.27	7.38	7.27	7.38	7.30
Mass concentration [mg.m^{-3}]							
NO_x	189	181	186	185	189	189	186
CO	2	2	2	2	3	3	2

The results of the measurements confirmed the accuracy of the selected settings described in chapter 4.2 and also the presumption of the interaction of primary deNOx methods in their combination.

5 Conclusions

The performed experiments, simulations and discussions pointed to several important aspects, as well as the facts about NOx reduction, verified by using a combination of primary methods in the limiting conditions of the thermal load of the combustion chamber.

The simulation model was developed to determine the characteristics of boiler operation and the efficiency of primary deNOx methods. This model was compared to the measurement results. The model showed a high degree of conformity in particular measured parameters.

The model has confirmed the predicted causes of excessive NOx formation, especially in the conditions of the extreme thermal load of the combustion chamber Q_v 0.3 MW/m^3. The results obtained by the standard primary methods of reduction of nitrogen oxides applied in this work, pointing to their effectiveness even under conditions of high thermal load in the combustion chamber, are as follows :

• Oxygen partial pressure – NOx decrease by 12.5%
• Cascade air supply – NOx decrease by 20%
• Water vapour injection – NOx decrease by 25% (the level of reduction was affected by boiler performance)
• Flue gas circulation – NOx decrease by 2%

The third stage of the research pointed to the problem of interactions of primary deNOx methods, especially the effectiveness of the reduction of individual methods. Thus, in the case of boiler operation according to the

settings from section 4.1, the NOx content was reduced by 45% to 190 mg/m^3. Further correlation of settings resulted in a further 3% reduction of nitrogen oxides.

The most effective method for NOx reduction has been the water vapour injection method. Vapour injection reduced the maximum temperature, eliminating the volume of high-temperature zones in the boiler combustion chamber by approximately 65%. Injecting approximately 100 kg of vapour per hour reduces NOx by 20 to 25% below the limit of 198 mg/m^3.

The most appropriate parameters of primary deNOx methods can be better identified by simulation programs than by direct measurements on the boiler because they are time efficient.

The results show that at present, the amount of NOx in large heat-producing plants will not be reduced by using just a single primary NOx reduction method. To successfully reduce NOx emissions in these units, a combination of two or more primary methods must be applied. According to the results presented in this paper, the best option is to use the following methods: (a) improve the circulation of gases in the combustion chamber, (b) adjust the partial pressure of oxygen, (c) inject water or steam or other compounds that lower the flame temperature, (d) adjusting the cascade supply of combustion air.

References

Adams T. (2016). Off-design point modelling of a 420 MW CCGT power plant integrated with an amine-based post-combustion CO₂ capture and compression process. *Applied Energy*, 178, pp. 681–702.

Anderson JD. (1995). Computational Fluid Dynamics: The Basics with Applications, 1st ed., Science, Engineering, Math. USA: McGraw-Hill Science, p.574.

Basu P, Kefa C and Jestin L. (1999). Boiler and Burners. Design and Theory. Berlin: Springer-Verlag

Ben Rejeb S. (2017). Thermal radiation modeling using the LES–ODT framework for turbulent combustion flows. *International Journal of Heat and Mass Transfer*, 104, pp. 1300–1316.

Boukhalfa N. (2016). Chemical Kinetic Modeling of Methane Combustion. *Procedia Engineering*, 148, pp. 1130–1136.

Bowman TC. (1992). Control of combustion – generated nitrogen oxid emissions: Technology driven by regulation. *Proc. of Combustion Institute*, 24(1), pp. 859-878.

Boxiong S. (2004). Kinetic model for natural gas reburning. *Fuel Processing Technology*, 85(11), pp. 1301–1315.

Dunn-Rankin D, Miyasato MM. and Trinh Pham K. (2008). Introduction and Perspectives. In Dunn-Rankin D (ed.) Lean Combustion Technology and Control. California, USA, pp. 1–18.

Dupláková D. and Husár J. (2014) Využitie simulácie procesov ako nástroj optimalizácie výrobných časov a nákladov. In:*Management of manufacturing systems 2014. Zborník vybraných vedeckých prác,* Starý Smokovec, TU of Košice, pp.32-37.

Durdán, M. and Kostúr, K. (2015). Modeling of temperatures by using the algorithm of queue burning movement in the UCG Process. *Acta Montanistica Slovaca*, 20(3), pp.181-191.

Fackler KB. (2015). NOx Behavior for Lean-Premixed Combustion of Alternative Gaseous Fuels. *Journal of Engineering for Gas Turbines and Power,* 138(4), p.11.

Fennimore CP. (1972). Formation of nitrik oxide from fuel nitrogen in ethylene flames. *Combustion and Flame*, 19(2), pp. 289-296.

Ferstl, K. and Masaryk, M. (2011). Heat transfer book. (Prenos tepla). 1st ed. Bratislava: Slovak University of Technology in Bratislava, p.424.

Fischer M. (2016). A chemical kinetic modelling study of the combustion of CH4–CO–H2–CO2 fuel mixtures. *Combustion and Flame*, 167, pp. 274–293.

Flagan, Richard C. and Seinfeld. (1988) *Fundamentals of air pollution engineering.* Prentice-Hall, Englewood Cliffs, New Jersey.

Flimel M. (2010). Problematika určovania skutočnej hodnoty súčiniteľa prechodu tepla stavebných konštrukcií budov metódou merania tepelného toku. *Vytápění, větrání, instalace*, 19(4), pp. 166-169.

Gavlas S, Lenhard R. and Jandacka J. (2013). Design and numerical simulation of the heat exchanger for heat recovery system with melting furnaces for melting secondary aluminums. In: Dancova, P., Novonty, P. (Eds.), *EFM12 - Experimental Fluid Mechanics 2012*, 7th International Conference on Experimental Fluid Mechanics (EFM), E D P SCIENCES, Cedex A, p. UNSP 01033.

Glarborg P. (1995). The thermal DeNOx process: Influence of partial pressures and temperature. *Chemical Engineering Science*, 50(9), pp. 1455-1466.

Gopalakrishnan P. (2007). *Controlling mechanisms for low NOx emissions in a non-premixed stagnation point reverse flow combustor*. Proceedings of the Combustion Institute, 31(2), pp. 3401–3408.

Gövert S. (2015). Turbulent combustion modelling of a confined premixed jet flame including heat loss effects using tabulated chemistry. *Applied Energy*, 156, pp. 804–815.

Gurevich, H.A. and Aksenov, V.L. (1976). *Investigation of the yield of nitrogen oxides in the furnace of the DKVR boiler with large excess air*. In the book: Formation of nitrogen oxides and ways to reduce their release into the atmosphere. Sb.nauch.tr. Kiev: Nauchna Dumka, pp.106-109.

Hayhurst AH. and Vince M. (1980). Progress in Energy and Combustion Science. Oxford Pergamon Press, 6, pp. 35-51.

Holoubek D. (2002) *Spaľovacie zariadenia, výmeníky tepla a kotly.* 1st ed. Košice, TU of Košice, p.2015.

Horbaj P. (2005). Some notes on basic parameters, determination of empirical formula and incineration of solid municipal waste. *Chemicke Listy*, 99(10), pp. 694-702.

Hua P. (2016). Promotional mechanism of propane on selective catalytic reduction of NOx by methane over In/H-BEA at low temperature. *Applied Surface Science*, 390, pp. 608–616.

Chen Z. (2017). Anthracite combustion characteristics and NOx formation of a 300 MWe down-fired boiler with swirl burners at different loads after the implementation of a new combustion system. *Applied Energy*, 189, pp. 133–141.

Choong-Kil S. (2011). De-NOx characteristics of a combined system of LNT and SCR catalysts according to hydrothermal aging and sulfur poisoning. *Catalysis Today*, 164(1), pp. 507–514.

Jablonský G, Pástor M and Dzurňák R. (2015). *Obohacovanie horľavej zmesi kyslíkom v praxi*. 1st ed. Košice: TU of Košice, p.92.

Jandacka J, et al. (2015). Performance and emission parameters change of small heat source depending on the moisture. *Manufacturing Technology*, 15(5), pp. 826-829.

Kristensen PG, Glarborg P. and Dam-Johansen K. (1996). Nitrogen Chemistry during Burnout in Fuel-Staged Combustion. *Combustion and Flame*, 107(3), pp. 211-222.

Lamoureux N. (2010). Experimental and numerical study of the role of NCN in prompt-NO formation in low-pressure CH4–O2–N2 and C2H2–O2–N2 flames. *Combustion and Flame*, 157(10), pp. 1929–1941.

Miller JA. and Glarborg P. (1996). Modeling the Formation of N2O and NO2 in the Thermal De-NOx Process. *Series in Chemical Physics*, 61, pp. 318-333.

Myles Bohon D. (2015). Experiments and simulations of NOx formation in the combustion of hydroxylated fuels. *Combustion and Flame*, 162(6), pp. 2322–2336.

Panda A, Prislupčák M. and Pandová I. (2014). Progressive technology diagnostic and factors affecting to machinability. *Applied Mechanics and Materials*, 616, pp. 183-190.

Panda A. (2011). Analysis of the process production. *Studia i materialy,* 29(2), pp. 22-28.

Rimar M. and Fedak M. (2014). Combustion processes. (Spaľovacie procesy.). 1st ed. Prešov: Technical University of Košice, p.144.

Rimar M. and Kulikov A. (2016). *NOx Formation in Combustion of Gaseous Fuel in Ejection Burner*, In: Lenhard, R., Kaduchova, K. (Eds.), Application of Experimental And Numerical Methods In Fluid Mechanics And Energy 2016: XX Anniversary of International Scientific Conference, Amer Inst Physics, Melville, p. 020051.

Saheed Ismail O. (2016). Modelling combustion reactions for gas flaring and its resulting emissions. *Journal of King Saud University - Engineering Sciences*, 28(2), pp. 130–140.

Salokyová Š. and Krenický T. (2016). Analysis of the effects of factors in relation to vibration of technological head during the splitting of construction steels through hydro-abrasive splitting. *Key Engineering Materials,* Volume 669, pp. 216-219.

Segal IJ and Lyubeznikov DA. (1966) The study of heat transfer gas torch at different degrees of pre-mixing the gas with air. *Inzhenerno Physics Journal*, 10, pp. 163-166.

Semenov NN (1929). Kinetics of Chain Reactions. *Chem.Rev.*, 61(3), pp.347-379.

Smeringai P, Rimár M. and Fedák M. (2015). Optimization of combustion process with respect to the assessment of nitrogen oxides formation. In: *Energetické premeny v priemysle 2015, Zborník vedeckých prác*. TU of Košice, pp. 190-194.

Smeringai P. and Rimár M. (2014). Simulácia procesov v spaľovacích zariadeniach s viacerými priemyselnými horákmi. In: *Management of Manufacturing Systems2014. Zborník vybraných vedeckých prác,* Starý Smokovec, pp.116-119.

Stephen Klippensteina J, Lawrence Hardinga B. and Glarborg P. (2011) The role of NNH in NO formation and control. *Combustion and Flame*, 158(4), pp. 774–789.

Terpák, J., Dorčák, Ľ. and Maduda, V. (2007). Combustion process modelling and control. *Acta Montanistica Slovaca,* 12(3), pp.238-242.

Trisjono P. (2016). Modeling turbulence–chemistry interaction in lean premixed hydrogen flames with a strained flamelet model. *Combustion and Flame*, 174, pp.194–207.

Van Oijen JA. (2016) State-of-the-art in premixed combustion modeling using flamelet generated manifolds. *Progress in Energy and Combustion Science*, 57, pp. 30–74.

Varga A, Kizek J. and Dudrik M. (2015). *Oxidačné činidlo v procese spaľovania*. 1st ed. Košice: TU of Košice, p.92.

Vyhláška Ministerstva životného prostredia SR č. 252/2016 Z. z., ktorou sa mení a dopĺňa vyhláška Ministerstva životného prostredia Slovenskej republiky č. 410/2012 Z. z., ktorou sa vykonávajú niektoré ustanovenia zákona o ovzduší v znení vyhlášky č. 270/2014 Z.z. [online] Available at: https://www.slov-lex.sk/static/pdf/2016/252/ZZ_2016_252_20161001.pdf [Accessed 2 May 2019].

Vyhláška Ministerstva životného prostredia SR č. 442/2013 Z.z., ktorou sa mení vyhláška Ministerstva pôdohospodárstva, životného prostredia a regionálneho rozvoja Slovenskej republiky č. 360/2010 Z. z. o kvalite ovzdušia. [online] Available at: https://www.slov-lex.sk/static/pdf/2013/442/ZZ_2013_442_20140101.pdf [Accessed 2 May 2019].

Westbrook KC. (2005). Computational combustion. *Proceedings of the Combustion Institute*, 30(1), pp. 125–157.

Wu Jeffrey CS. (2013). Removal of NOx by photocatalytic processes. *Journal of Photochemistry and Photobiology. C: Photochemistry Reviews*, 14(1), pp. 29–52.

Wünning JA. and Wünning JG. (1997). Flameless oxidation to reduce thermal no-formation. *Progress in Energy and Combustion Science*, 23(1), pp. 81-94.

Xubo G. (2016) Modeling and simulation of urea-water-solution droplet evaporation and thermolysis processes for SCR systems. *Chinese Journal of Chemical Engineering*, 24(8), pp. 1065–1073.

Yeh CL. (2013). NOx Reduction in a Carbon Monoxide Boiler by Reburning. *Procedia Engineering*, 67, pp. 378-387.

Yeromin, A., Yeromina O., Lukáč L., Kizek J. and Dzurňák R. (2018). The possibility of increasing the efficiency of temperature distribution control in reheating furnaces. *Acta Montanistica Slovaca*, 23(2), pp.175-183.

Young Kim H. (2012) Investigation of fuel lean reburning process in a 1.5 MW boiler. *Applied Energy*, 89(1), pp. 183–192.

Yu JCC. (2016). NOx abatement from stationary emission sources by photo-assisted SCR: Lab-scale to pilot-scale studies. Applied Catalysis, A: General, 523, pp.294–303.

Zajac J. and Čorný I. (2004). *Monitoring of processing fluids*. Science Report, Kielce, pp. 215-229.

Zel'dovich BJ and Frank-Kamenetskiy DA. (1947). *The oxidation of nitrogen during the combustion*. Kyiv: Nauka, p.146.