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Mathematical Modelling for Control Configuration of NO_X Formation in Coal Combustion Processes

KEYWORDS: coal combustion, mathematical modelling, formation of NO_x

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ABSTRACT *The paper deals with the problems concentrated on formation of the most important types NOx. The main part of paper describes the Zeľdovič model of creation NO in coal and some results from mathematical calculations.*

1. INTRODUCTION

Oxides of nitrogen, designated as NO_x, generally include NO (nitrogen monoxide, that is also known as nitric oxide) and NO_2 (nitrogen dioxide) are investigated numerically using a finite volume method for the solution of the conservation and reaction equations governing the problem predicting NO_x emissions from the combustor good agreement with the experimental measurements.

2. EMISSIONS OF NITROGEN OXIDES AS ONE OF MAJOR AIR POLLUTANTS

Pollutants are usually classified into several groups according their toxicity, spread, potential danger and emission sources. Nitrogen oxides together with sulphur dioxide, carbon monoxide, hydrocarbons, solid particles and photochemical oxides belong to major (critical) air pollutants. Nitrogen oxides, as primary air pollutants, are formed predominantly by the high/temperature fixation of nitrogen and oxygen in power plants and combustion equipment.

Fig.1 shows contribution of individual gases (Sulphur dioxide, Nitrogen oxides, Carbon monoxide) on emissions of major air pollutants in the years from 2011 to 2012. The measured values of Nitrogen oxides range from 105.6 thousand Tons/Year to 82.8 thousand Tons/Year.

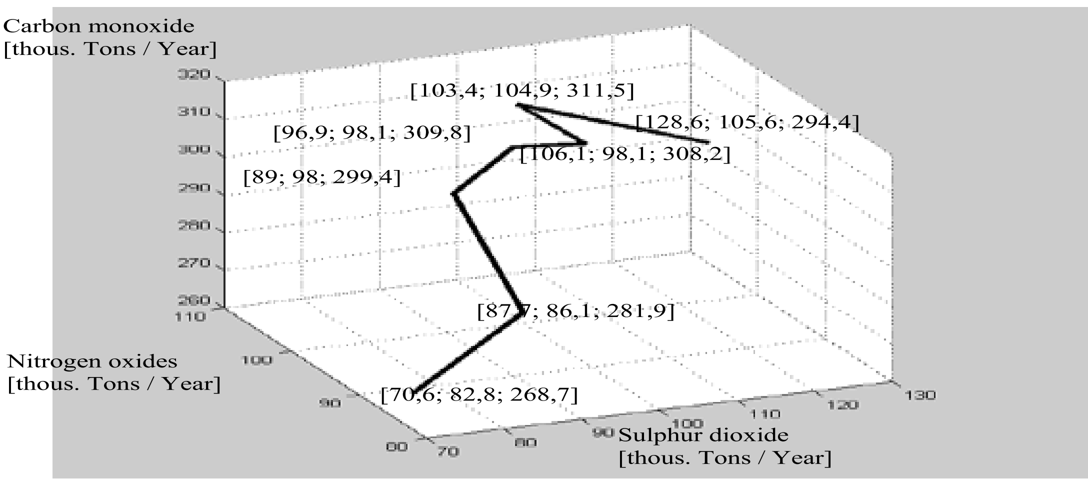

Fig.1 Contribution of individual gases (Sulphur dioxide, Nitrogen oxides, Carbon monoxide) on emissions of major air pollutants in the years from 2011 to 2012.

It is essential, that permanent economic growth has a negative influence on the quality of environment. Tightening environmental regulations increase the possibility for sustainable development of natural sources. It is also a motivation for development of both science and innovations in entrepreneur activities. Environmental protection is also reflected in a number of investments of both enterprises and municipalities.

3. CONTROL OF NO_X FORMATION

NO_x formation depends especially on:

- temperature,
- oxygen partial pressure,
- coal properties.

One of the coal properties that might be important for NO_x formation is content of nitrogen in it. Also every boiler is specific from the view point of low NO_x combustion techniques implementation. Let us mention some of the different approaches to reduce the NO_x emissions from the boiler [2]:

- the burner quality (low NO_x burner),
- fuel reburning,
- air staging in furnace,
- recirculation of gas flue.

3.1 NO_x formation using coal reburning technology in industrial boilers

Coal reburning technology is one of those that try to set control of both CO_x and NO_x formation during the burning process in industrial boilers. Fig. 2 shows the technology where we can recognize three zones with the typical reactions. Both burning and reburning are sophisticated processes that are influenced also by the fuel quality. Some of the approximate reactions of burning and reburning processes are mentioned in the following [3].

Fuel combustion and NO_x formation are typical reactions for primary combustion zone:

$$N\ (fuel) + O_2 \rightarrow NO_x \quad (1)$$

$$N_2\ (air) + O_2 \rightarrow NO_x \quad (2)$$

In general:

$$Fuel + O_2 \rightarrow CO_2 + CO + H_2O + Other\ Species \quad (3)$$

Using the Zel’dovič mechanism [4], NO production can be expressed as (5):

$$\frac{d[NO]}{d\tau} = \frac{1}{1+\frac{k_{-3}.[NO]}{k_4.[O_2]+k_5.[OH]}} . \left[2.k_3.[N_2].[O] - \frac{2.k_{-3}.k_{-4}.[NO]^2.[O]}{k_4.[O_2]+k_5.[OH]} - \frac{2.k_{-3}.k_{-5}.[NO]^2.[H]}{k_4.[O_2]+k_5.[OH]} \right] \quad (4)$$

Using some approppriate mathematical modification [6],[7]:

$$\frac{d[NO]}{d\tau} = \frac{2.[O].\left(k_3.k_4.[O_2].[N_2] - k_{-3}.k_{-4}.[NO]^2\right)}{k_4.[O_2] + k_{-3}.[NO]}, \tag{5}$$

where k_3, k_4, k_5, k_{-3}, k_{-4}, k_{-5} are rate constants with values given in $cm^3.mol^{-1}.s^{-1}$:

$$k_3 = 1{,}36.10^{14}.e^{-\frac{75400}{R.T}}$$

$$k_4 = 6{,}43.10^{9}.T.e^{-\frac{6250}{R.T}}$$

$$k_{-3} = 3{,}1.10^{-3}.e^{-\frac{334}{R.T}}$$

$$k_{-4} = 1{,}55.10^{9}.T.e^{-\frac{38640}{R.T}}$$

Reburning technology, that is applied in industrial boilers, is based on steam injection into the reburning zone. Using the reburning techniques allows optimization of both combustion (flue) gas and air to control both CO and NO_x formation. Reburning technology is a process that uses hydrocarbon radicals and catalyst to covert nitrogen oxide (NO) to nitrogen (N_2) and carbon dioxide (CO_2):

$$2NO + 2CO + catalyst = N_2 + 2CO_2 \tag{6}$$

In general:

$$\text{Reburn Fuel} \rightarrow CH_x + \text{Other Species} \tag{7}$$

$$CH_x + NO_x \rightarrow \bullet CN + \bullet NH_2 + H_2O \tag{8}$$

$$NO_x + \bullet CN \rightarrow N_2 + CO \tag{9}$$

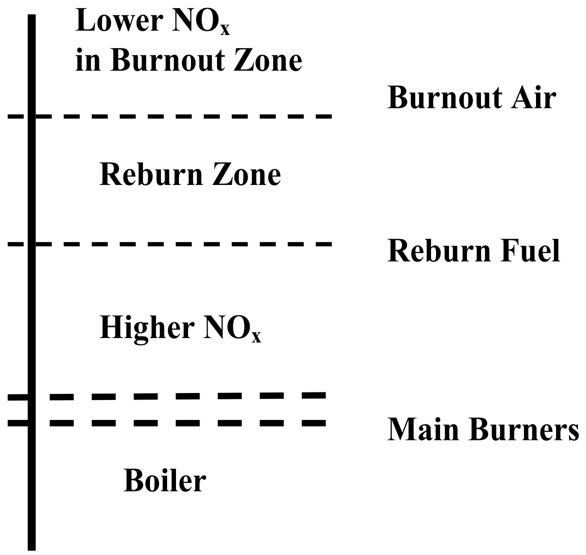

Fig.2 Levels of burning processes in reburn technology with the stress on NO_x formation representation.

Typical processes in Burnout zone can be expressed by the reactions [8], [9]:

$$Air + CH_x + CO \rightarrow CO_2 + H_2O \tag{10}$$

$$\bullet CN + \bullet NH_2 + O_2 \rightarrow NO_x + CO_2 + H_2O \tag{11}$$

Taking into account reactions (10) and (11), it is clear, that if there is not enough air in the reaction (10), CO remains. If there is too much oxygen in the reaction (11), greater amount of NO_x is formed in the burner. Optimization of the amount of air and oxygen, during the appropriate temperature, is one of the ways to control both CO and NO_x formations [10].

4. MATHEMATICAL MODELLING FOR OPTIMIZATION OF THE RELATIONSHIPS BETWEEN AIR, OXYGEN, TEMPERATURE AND NO_X FORMATION

Chosen values for amount of air excess, temperature, oxygen and NO_x obtained during the experimental measurements on pulse burner are used to find common relationships and specify constraints for NO_x formation [11].
Using the method of multiple regression, we will try to express common relationship among amounts of air excess, temperature, oxygen and NO_x formation.

Let be use the following signification:

x_1 … air excess,
x_2 … temperature in ºC,
x_3 … oxygen in $mol.cm^{-3}$,
y … NO_x in $mol.cm^{-3}$.

Assuming the linear relationship, we can express:

$$\hat{y} = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 \tag{12}$$

$$\left| y_1 - \hat{y}_1 \right| \tag{13}$$

The squares of residuals would be expressed as [12],[13]:

$$S(a_0, a_1, a_2, a_3) = \sum_{i=1}^{n} \left(y_i - \hat{y}_i \right)^2 = \sum_{i=1}^{n} \left(y_i - a_0 - a_1 x_{1i} - a_2 x_{2i} - a_3 x_{3i} \right)^2 \tag{14}$$

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Table 1. Casewise Diagnostics with the residuals computed using the program system SPSS. Casewise Diagnostics[a]

Case Number	Std. Residual	NOx	Predicted Value	Residual
1	-1,275	,00000000375299	7,226727907167759E-9	-3,473737907167760E-9
2	2,128	,00000000986418	4,064593011073113E-9	5,799586988926887E-9
3	-,325	,00000000157045	2,456799226605485E-9	-8,863492266054848E-10
4	,031	,00000000191858	1,832806803389715E-9	8,577319661028473E-11
5	,118	,00000000206717	1,745400717720162E-9	3,217692822798382E-10
6	,041	,00000000206839	1,957495267974767E-9	1,108947320252328E-10
7	-,093	,00000000194660	2,199900874642326E-9	-2,533008746423262E-10
8	-,316	,00000000179162	2,653121987299688E-9	-8,615019872996883E-10
9	-,554	,00000000161116	3,120816444619380E-9	-1,509656444619380E-9
10	-,757	,00000000150157	3,563807055124524E-9	-2,062237055124524E-9
11	-,983	,00000000127801	3,956554801486063E-9	-2,678544801486063E-9
12	-1,154	,00000000113328	4,278883946127 95E-9	-3,145608394612795E-9
13	1,929	,00000000978004	4,521867703494209E-9	5,258172296505791E-9
14	1,280	,00000000816945	4,681686598011462E-9	3,487763401988538E-9
15	,664	,00000000655869	4,749116475334722E-9	1,809573524665279E-9
16	,413	,00000000584794	4,722254270404578E-9	1,125685729595423E-9
17	-,101	,00000000433061	4,605829523296332E-9	-2,752195232963324E-10
18	-,182	,00000000380282	4,297573177043346E-9	-4,947531770433461E-10
19	-,279	,00000000325853	4,018884206156219E-9	-7,603542061562190E-10
20	-,586	,00000000205153	3,649485554543238E-9	-1,597955554543238E-9

a. Dependent Variable: NOx

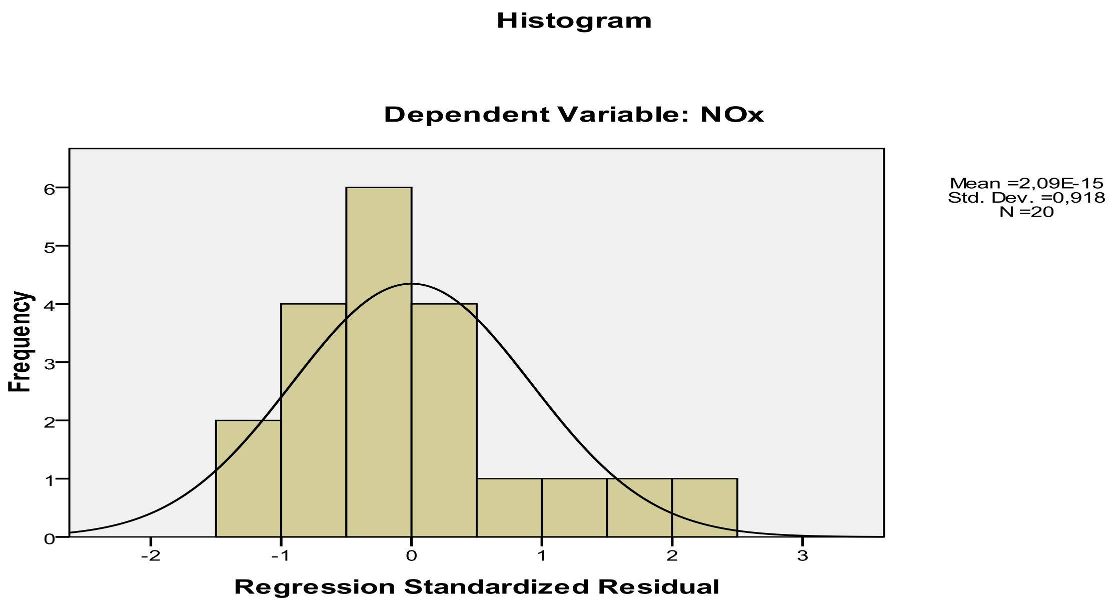

Fig.3 Histogram for dependent variable NO_x with the value of mean and standard deviation.

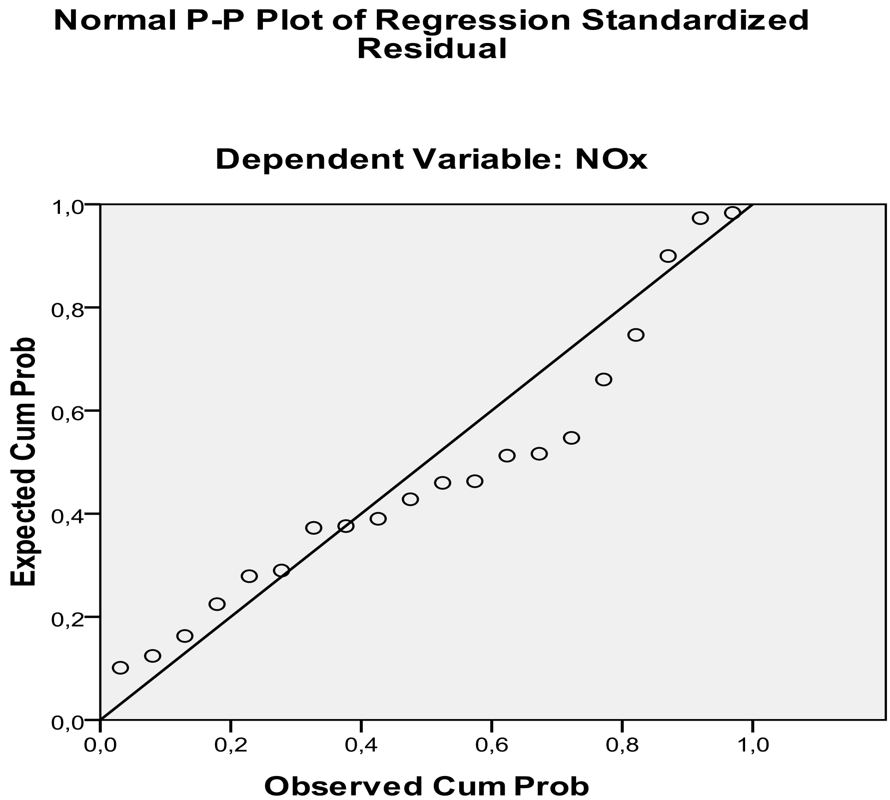

Fig.4 Normal P-P plot of regression standardized residual for dependent variable NO_x.

To fined the proper values for the coefficients: a_0, a_1, a_2 and a_3 the sum (14) should be minimized:

$$\frac{\partial S(a_0,a_1,a_2,a_3)}{a_0} = 2\sum_{i=1}^{n}(y_i - a_0 - a_1x_{1i} - a_2x_{2i} - a_3x_{3i}).(-1)$$
$$\frac{\partial S(a_0,a_1,a_2,a_3)}{a_1} = 2\sum_{i=1}^{n}(y_i - a_0 - a_1x_{1i} - a_2x_{2i} - a_3x_{3i}).(-x_{1i})$$
$$\frac{\partial S(a_0,a_1,a_2,a_3)}{a_2} = 2\sum_{i=1}^{n}(y_i - a_0 - a_1x_{1i} - a_2x_{2i} - a_3x_{3i}).(-x_{2i}) \quad (15)$$
$$\frac{\partial S(a_0,a_1,a_2,a_3)}{a_3} = 2\sum_{i=1}^{n}(y_i - a_0 - a_1x_{1i} - a_2x_{2i} - a_3x_{3i}).(-x_{3i})$$

Let each derivative equal zero, then (Abrikosov,1975):

$$na_0 + \sum_{i=1}^{n}x_{1i}.a_1 + \sum_{i=1}^{n}x_{2i}.a_2 + \sum_{i=1}^{n}x_{3i}.a_3 = \sum_{i=1}^{n}y_i$$
$$\sum_{i=1}^{n}x_{1i}.a_0 + \sum_{i=1}^{n}(x_{1i})^2.a_1 + \sum_{i=1}^{n}x_{1i}x_{2i}.a_2 + \sum_{i=1}^{n}x_{1i}x_{3i}.a_3 = \sum_{i=1}^{n}x_{1i}y_i$$

$$\sum_{i=1}^{n} x_{2i} a_0 + \sum_{i=1}^{n} x_{1i} x_{2i}.a_1 + \sum_{i=1}^{n} (x_{2i})^2.a_2 + \sum_{i=1}^{n} x_{2i} x_{3i}.a_3 = \sum_{i=1}^{n} x_{2i} y_i \qquad (16)$$

$$\sum_{i=1}^{n} x_{3i}.a_0 + \sum_{i=1}^{n} x_{1i} x_{3i}.a_1 + \sum_{i=1}^{n} x_{2i} x_{3i}.a_2 + \sum_{i=1}^{n} (x_{3i})^2.a_3 = \sum_{i=1}^{n} x_{3i} y_i$$

Solving the system of linear equations (16), we can get the values for the coefficients: a_0, a_1, a_2 and a_3. There are many methods to do so. The program system SPSS was used (Table 3) together with the setting the Pearson correlations (Table 2).

Table 2. Pearson Correlations computed using the program system SPSS. (Correlations)

		NOx	Air	Temperature	Oxygen
Pearson Correlation	NOx	1,000	,132	-,105	-,334
	Air	,132	1,000	-,991	-,777
	Temperature	-,105	-,991	1,000	,694
	Oxygen	-,334	-,777	,694	1,000

Table 3. Values: a_0 as a constant and coefficients a_1, a_2, a_3 computed using the program system SPSS.

Model		Unstandardized Coefficients	Standardized Coefficients	t	Sig.
1	(Constant)	1,581E-7		1,314	,207
	Air	-4,456E-8	-4,647	-1,263	,225
	Temperature	-4,522E-11	-3,805	-1,181	,255
	Oxygen	-,031	-1,300	-1,856	,082

Partial dependences are expressed on graphs: Fig. 3, Fig. 4 and Fig. 5.

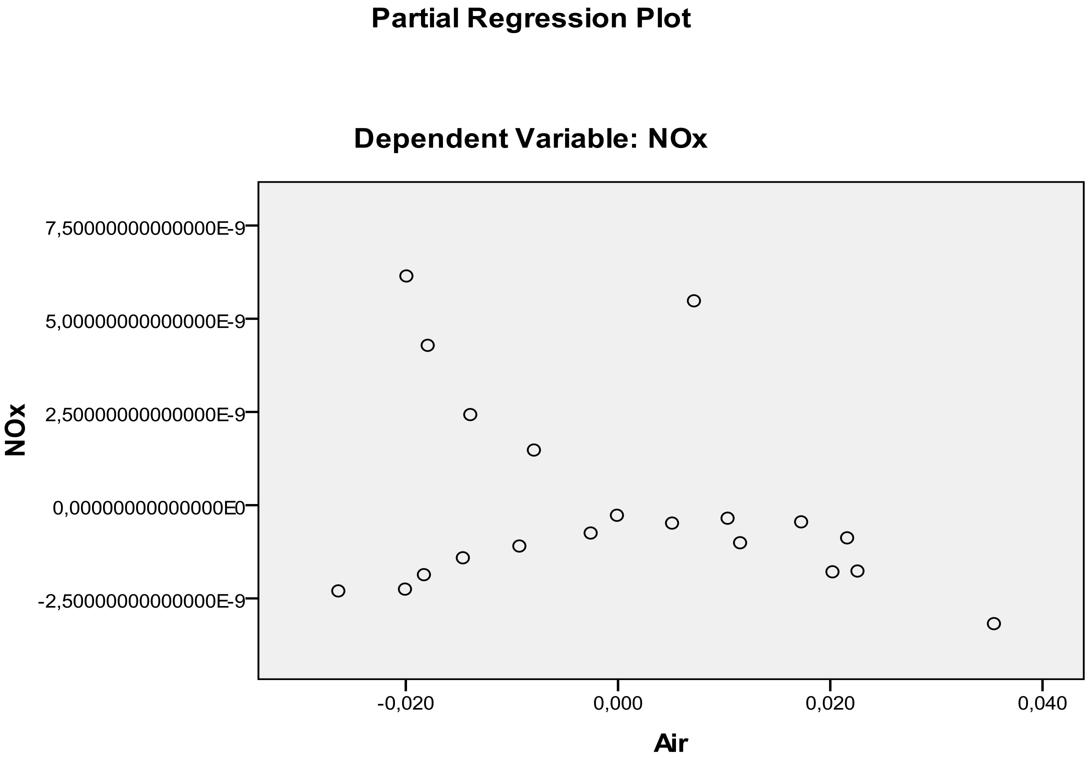

Fig.5 Partial regression plot, that expresses dependences between amounts of air excess and NO_x formation using the program system SPSS.

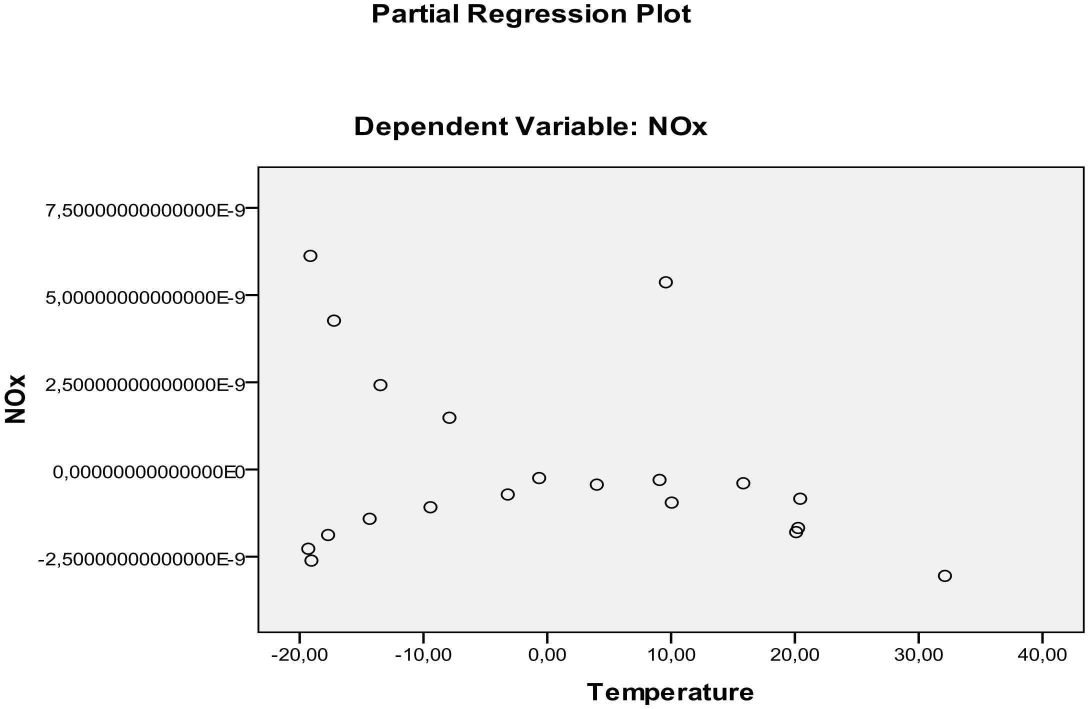

Fig.6 Partial regression plot, that expresses dependences between temperature and NO_x formation using the program system SPSS.

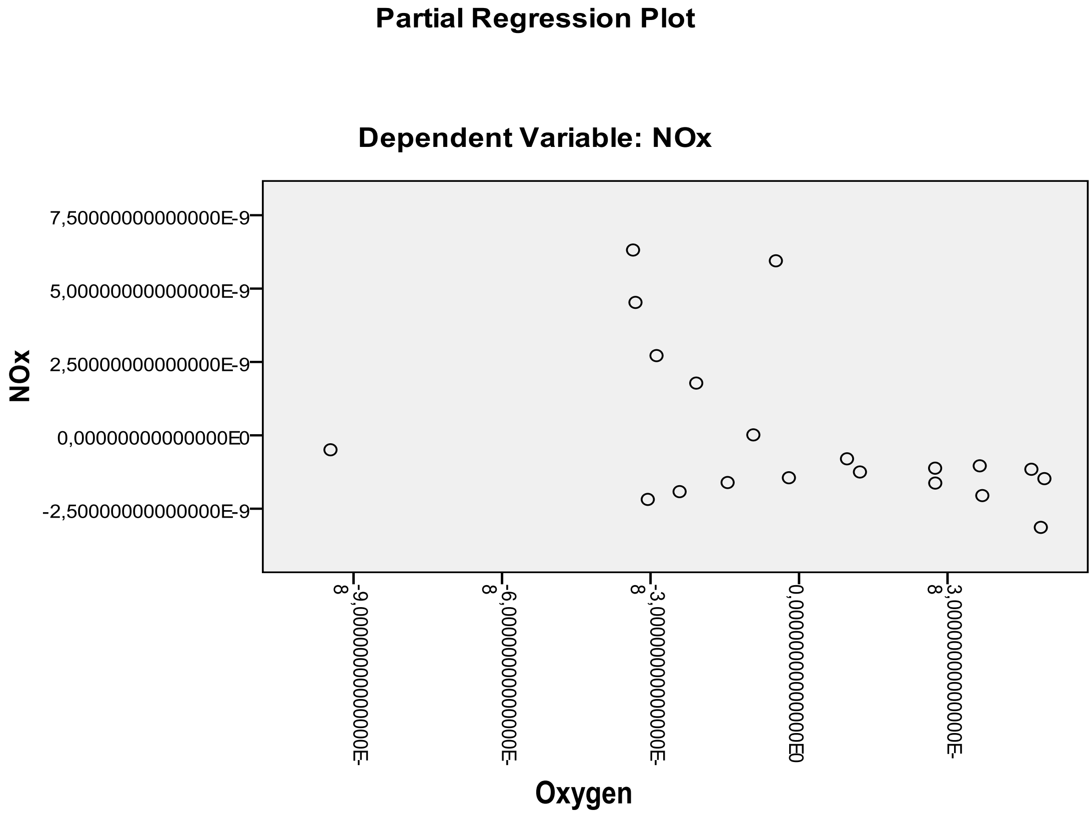

Fig.7 Partial regression plot, that expresses dependences between amounts of oxygen and NO_x formation using the program system SPSS.

Conclusion

Mathematical modelling was used to describe some processes of chemical reactions which are typical for industrial boiler aiming especially to control the formation of some pollutants, such as NO_x and CO [14]. Control of both NO_x and CO formations during burning and reburning processes can be easier knowing the relationships among the amounts of air excess, oxygen, temperature and NO_x formation [15]. The common relationship is expressed in (12) and Table 3 comprises the concrete values of a_0 and coefficients a_1, a_2, a_3, that were obtained using the program system SPSS.

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