

INFLUENCE OF FURNACE COMBUSTION CONDITIONS ON NO_x EMISSION FROM LIGNITE FLAMES

Života Kostić, Banislav Repić, Dragoljub Dakić and Ljubomir Jovanović

*INSTITUTE OF NUCLEAR SCIENCES - Vinča
Laboratory for Thermal Engineering and Energy
11001 BELGRADE, P.O.Box 522, YUGOSLAVIA*

ABSTRACT

Coal combustion in boiler furnaces is followed by emission of pollutants, i.a. NO_x compounds. The appropriate activities have been conducted lately for lowering this emission and satisfying the ecology requirements. Therefore, the knowledge of NO_x formation mechanism in furnace conditions is of great importance.

In the paper presented are the results of an application of the developed model on the computation of the chemithermodynamic equilibrium of a system formed by compounds and elements contained in the Kolubara basin lignite and the combustion air, at temperatures from 800 to 1700 K, pressure 1 bar, for two lignite compositions at excess air $\alpha = 1.25$. The briefly outlined developed mathematical model used for shaping the computation algorithm takes into account only the thermal oxides formation mechanism which is for Kolubara lignites, having low nitrogen content, the dominant NO_x formation mechanism even at lower combustion temperatures.

The results obtained are of use, as thermodynamic indicators, for lowering NO_x emission by adequately organizing and conducting the combustion process, i.e. by preventing formation of temperature zones with NO_x emission above the allowed values. A sample computation of the equilibrium composition of the system has been performed for the stoichiometric combustion case, thus illustrating the possibility of NO_x emission lowering by applying the so-called sub-stoichiometric combustion.

INTRODUCTION

Yugoslav lignites (from Kolubara and Kosovo basins) have relatively low sulphur content (below 1%, combustible sulphur below 0.5%). This fact gives the problem of lowering the NO_x emission the same or even greater significance than lowering the SO₂ emission. Considering the fact that the existing lignite fueled thermal power plants exceed 5000 MW electric power and that construction of new

ones continues, one can estimate the great significance of investigating and developing the new activities and methods of lowering the NOx emission. It is possible to reduce the NOx content in flue gases by refining them and as well by conducting the combustion process in such a way as to reduce the NOx production; the latter being more natural. For determining the appropriate way of conducting the combustion process, one needs to analyze the influence of temperature upon the NOx formation.

Three mechanisms of NOx formation are known: (1) by oxidation of the atmospheric molecular nitrogen, (2) by oxidation of fuel nitrogen, and (3) by formation of prompt NOx by reaction of fuel fragments with the molecular nitrogen. Prompt nitrogen oxides account for less than 10 ppm and usually are of no significance in practical combustors /7/. Depending the nitrogen content in the fuel, fuel NOx can account for 35-80% of total NOx formed in the pulverized coal combustion /7/. However, for lower values of fuel nitrogen content (below 0.7%) the so-called thermal NOx, formed by oxidation of molecular nitrogen, become dominant. Experimental measurements /8/ conducted at Kosovo TPP's, fueled by Kosovo lignite, have confirmed that the thermal NOx dominate the total NOx emission.

The computation of chemithermodynamic equilibrium of the system formed by elements and compounds contained in coal and combustion air, yields the equilibrium composition of flue gases with respect to the combustion temperature. Based upon that, for the case of thermal NOx dominating the total NOx emission, it is apt to analyze the influence of temperature upon the formation of NOx (and other pollutant gases) and the possibility of lowering the NOx emission by adequately conducting the combustion process within the furnace. The computations, the results of which are presented here, are performed for coal composition of Kolubara lignite taken from a mill feeder and air with an excess air ratio of $\alpha = 1.25$. A sample computation is performed for the stoichiometric combustion case, thus illustrating the possibility of lowering the NOx emission by applying the so-called sub-stoichiometric combustion.

THE COMPUTATION

Equations used to model the thermodynamic equilibria of systems with on-going chemical reactions may be formulated by using two approaches. The first one is based on the minimization of (Gibbs) free energy /1/. The second approach, used to model and develop the algorithm used for thermodynamic computations the results of which are presented here, is based upon the mass action law (method of the reaction constants).

The first step in chemical equilibria thermodynamical modeling is the decision on the number of gas and condensed (solid or liquid) phase species to be considered. If this number is m , the number of dense (solid and liquid) phase species is f and the number of atomic species is q , then $m-q$ mass action law equations determine the equilibrium composition. In other words, $m-q$ equilibrium constants pertain. The equilibrium constants are usually specified for decomposition reactions down to constituent atoms, all the equations being thus independent

$$K_j = \prod_{i=1}^q (p_i^{a_{ij}} / p_j) \quad (j = 1, 2, \dots, m-q) \quad (1)$$

where p_i are the atomic species partial pressures, p_j the molecular species partial pressures, a_{ij} the decomposition reaction stoichiometric coefficient matrix, and K_j the mass action constants of decomposition reactions down to atoms.

For an ideal gas mixture, the Dalton law is introduced into the thermodynamic equilibrium equations:

$$\sum_{j=1}^m p_j = p \quad (2)$$

In the work reported here the gas phase is considered solely. In cases considering condensed phases too, the system of thermodynamic equilibrium equations is added with stress coefficients of the vapour above the condensed phases of given chemical type at the temperature considered, and balance equations of those atoms in the system which appear in the condensed phases. Details on this can be found e.g. in reference /2/.

Ya.B.Zel'dovich /3/ has shown that the mass action and conservation law system of equations has only one real positive solution for a specific parameters set. The thermodynamic equilibrium system of equations (1) and (2) is a non-linear system of algebraic equations usually solved iteratively starting from a selected set of initial values for the major constituents, by the Seidel's (m-1 species partial pressure initial approximation) method, the Newton's method or some other. If the Newton's method is to be used, the system of equations has to be linearized first. This may be done either by means of Taylor's expansion for unknown partial pressures where-by the second and higher order terms are neglected or by taking the logarithm of the initial set of equations and then solving for the logarithms of the unknown quantities.

In the work reported here, the straightforward iterative method was used to obtain the solution of equations (1) and (2). The initial set of values of partial pressures for the major constituent species (N_2 , H_2O , CO_2 , SO_2 , O_2) are specified only. Solution progresses from the lower temperature (800 K), with the temperature increment $\Delta T = 25$ K. Partial pressure of the component with the highest content in flue gases (N_2 in our case) was determined in all consequent iterations from Dalton law; so as to eliminate the appearance of negative values.

The coefficients of the polynomial describing the dependence of the (Gibbs) free energy on the temperature and enthalpy change in chemical reactions, used in the computation of equilibrium constants, are found in reference /6/.

COMPUTATIONAL RESULTS

The computation was performed for eight compositions of Kolubara lignite, taken from a mill feeder in operation at a 110 MW unit at Kolubara TPP, with characteristics obtained from proximate and elementary analyses, presented in Tab.1.

Excluding ash, all other constituents given in Tab.1 are present in flue gases after combustion. The elementary composition of the gas phase, for eight lignite compositions given in Tab.1, after combustion with an excess air ratio of $\alpha=1.25$, is presented in Tab.2 with the ordinal numbers 1-8 respectively. No 9 in Tab.2 represents the elementary composition of the gas phase after the combustion of lignite No 1 (Tab.1) with the stoichiometric quantity of air (more precise with a slight excess oxygen, i.e. for the condition of constant partial pressure of oxygen in flue gases equal to 10 bar). The excess air coefficient was calculated with respect to the stoichiometric air quantity needed for combustion of carbon, combustible sulphur, and hydrogen (values given in Tab.1) to form CO_2 , SO_2 and H_2O , respectively.

The results of computation of the chemithermodynamic equilibrium of the system No 1 (Tab.2) are presented in Fig.1. The numerical values are plotted for all

gas constituents of flue gases with partial pressures exceeding $10E-10$ bar. Considering pollutants only there are significant amounts of SO_2 , NO and at lower temperatures SO_3 . Obviously, presence of NO_2 and N_2O is negligible and there are no other nitrogen oxides, i.e. their partial pressures remaining much below $10E-10$ bar.

Tabela 1. Composition of the raw Kolubara coal (%)

No	Moisture	Ash	C	H	Scomb.	N	O
1	50.90	19.50	20.04	1.89	0.32	0.35	7.00
2	54.60	11.00	22.87	2.06	0.23	0.43	8.80
3	48.50	16.94	22.55	2.20	0.28	0.32	9.21
4	51.70	14.33	22.53	2.19	0.24	0.30	8.71
5	52.80	14.08	22.29	2.16	0.24	0.28	8.15
6	51.00	16.74	21.61	1.86	0.28	0.28	8.23
7	52.90	13.64	22.41	1.94	0.29	0.29	8.53
8	49.60	18.96	21.09	1.95	0.31	0.27	7.82

In Fig.1 (the same approach was taken in the other Figures) marked are the required limits for SO_2 and NO_x emission according to German regulations /4/. Dashed line 1 represents the values of SO_2 partial pressure corresponding to SO_2 emissivity limit for solid fuels, $400 \text{ mg}/\text{Nm}^3$. Dash-dot lines represent the partial pressures corresponding to NO_x emissivity limits, for existing TPP boilers (line 2, 390 ppm , corresponding to $800 \text{ mgNO}_2/\text{Nm}^3$) and for new coal fueled boilers (line 3, 97.5 ppm , corresponding to $200 \text{ mgNO}_2/\text{Nm}^3$).

From Fig.1 it is obvious that NO_x emission is highly sensitive to lignite combustion temperature, increasing with it, and at 1300 K exceeds the NO_x limit for new boilers, and at 1560 K the NO_x emission exceeds $800 \text{ mgNO}_x/\text{Nm}^3$.

Fig.1 presents the experimental results of the NO_x emission measured at 210 MW , 308 MW and 620 MW units at the Nikola Tesla TPP (Obrenovac) and at 32 MW and 110 MW units at the Kolubara TPP (Veliki Crljeni), all units fueled with the pulverized Kolubara lignite. Singular points (Fig.1) represent the average values of the NO_x emission in the 1986-1990 period /9/.

In reference /5/ a review of methods for lowering the NO_x formation at TPP's is presented. The essence of all these methods is to induce, by means of the appropriate methods, the lowering of temperature in certain boiler segments where it exceeds, for the case in Fig.1, 1300 K , thus reducing the NO_x emission, or ensuring the combustion with sub-stoichiometric quantity of oxygen in the high-temperature zones. The SO_2 emission cannot be influenced significantly by furnace temperature variation because it is practically constant above 1100 K and depends mostly upon the content of combustible sulphur in the coal.

Fig.2 presents the results of the computation of NO , SO_2 and SO_3 equilibrium concentrations for systems 1-8 (Tab.2). By comparing these results with the ones in Fig.1 one observes that only the SO_2 varies depending on the combustible sulphur content, whereas for NO_x the computation yielded in all cases practically the same values at the same temperatures. In this case the partial pressure values above $10E-5$ are presented only. Other compounds, including NO_2 and N_2O , have partial pressure values close to the values presented in Fig.1.

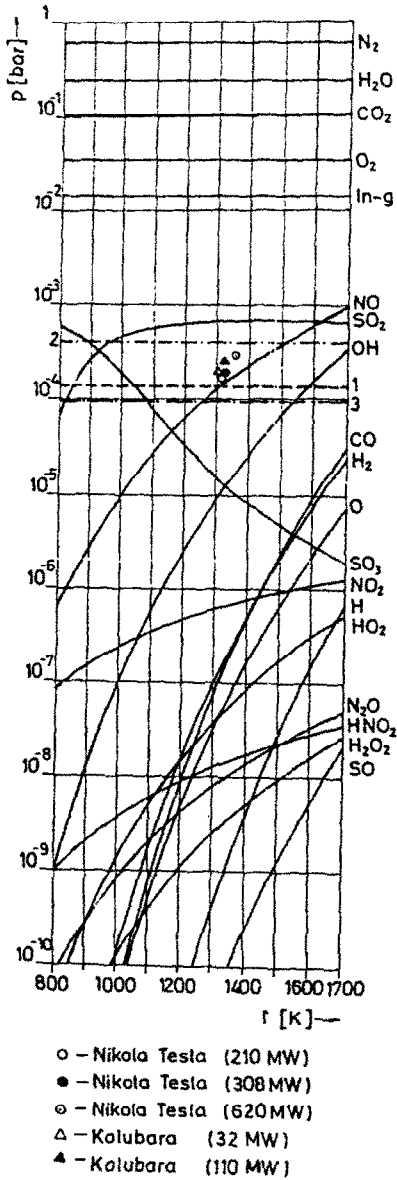


Fig.1 - Equilibrium composition of the system No 1 (Tab.2)

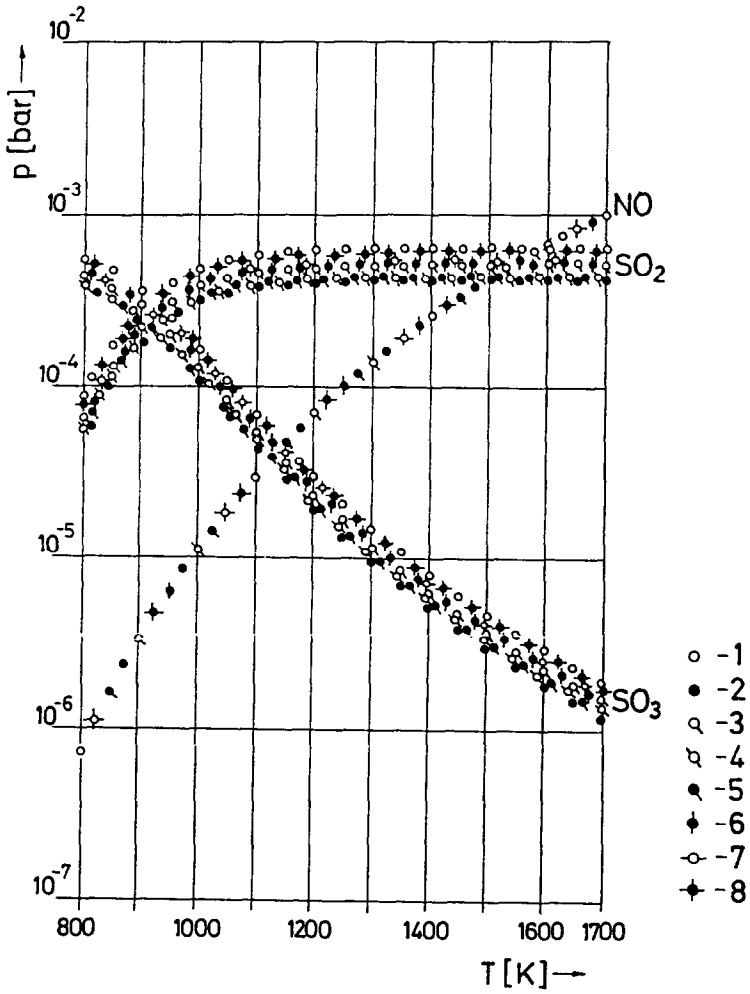


Fig.2 - Partial pressure of NO, SO₂ and SO₃ for the systems No 2-8 (Tab.2)

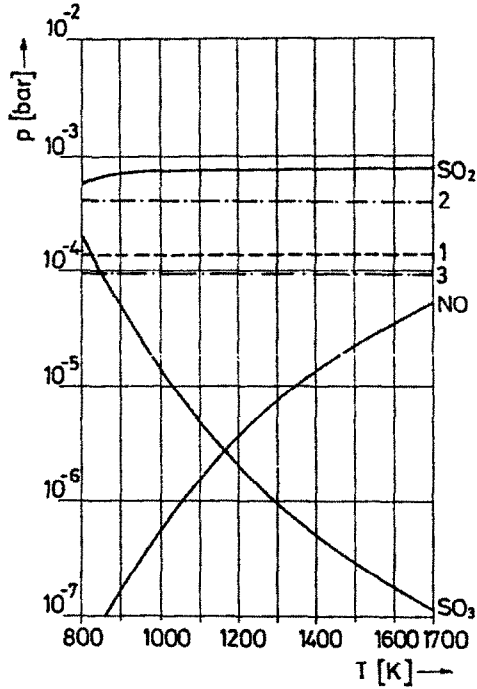


Fig.3 - Partial pressure of NO, SO_2 and SO_3 for the system No 9 (Tab.2)

Tabele 2. Gramm-atom fractions in elementary composition of combustion gases

No	α	H	C	S	O	N	Inert gases
1	1.25	0.20883	0.04630	0.00028	0.22735	0.51094	0.00630
2	1.25	0.20303	0.04770	0.00018	0.22761	0.51513	0.00635
3	1.25	0.19280	0.04840	0.00022	0.22483	0.52746	0.00629
4	1.25	0.19971	0.04756	0.00019	0.22597	0.52036	0.00621
5	1.25	0.20237	0.04712	0.00019	0.22614	0.51800	0.00618
6	1.25	0.20109	0.04840	0.00023	0.22820	0.51592	0.00616
7	1.25	0.20116	0.04834	0.00023	0.22812	0.51599	0.00616
8	1.25	0.20105	0.04765	0.00026	0.22674	0.51794	0.00618
9	1.00	0.24346	0.05398	0.00032	0.23033	0.46617	0.00574

Fig.3 presents the results of the computation of equilibrium composition for the stoichiometric combustion of lignite No 1 (Tab.1), i.e. for the system No 9 (Tab.2); the computation performed for low excess oxygen, i.e. for the case of constant O₂ pressure (10E-4 bar). The results indicate that stoichiometric combustion can lower the NO_x emission below the allowed limit. In USA, the method of sub-stoichiometric combustion is used for prompt temporary lowering of the NO_x emission below the allowed limits.

CONCLUSION

This paper presents a mathematical model utilized for forming an algorithm for computation of the thermodynamic equilibrium of a coal-air system, for eight compositions of Kolubara lignite combusting with an excess air coefficient of $\alpha=1.25$. The obtained results can be used as the thermodynamic indicators useful for the NO_x emission lowering by adequately organizing and conducting the combustion process, i.e. by preventing the creation of high temperature zones with the NO_x emission above the allowed limit. A sample computation of the equilibrium composition of the system has been performed for the stoichiometric combustion case, thus illustrating the possibility of lowering the NO_x emission by applying the so-called sub-stoichiometric combustion.

REFERENCES

1. W.B.White, S.M.Johnson & G.B.Dantzig:
Chemical Equilibrium in Complex Mixtures; *J.Chem.Phys.*, 28, 5, pp.751 (1958).
2. Ž.G.Kostić, P.B.Pavlović & P.Lj.Stefanović:
Thermodynamic Studies of High Temperature Equilibria of the Si-N, Si-C-H and Si-O-C-H Systems; *Colloque C5, supplement au Journal de Physique*, No 18, C5-11, C5-17 (1990).
3. Ya.B.Zel'dovich:
Dokazatel'stvo yedinstvennosti resheniya uravnenii deistvuyushchikh mass;
Zhurnal fizicheskoi khimii, T.2, vip.5, pp.685 (1938).
4. *Tehnička uputstva za očuvanje čistoće vazduha*; Izd. Savez društava za čistoću vazduha Jugoslavije, Sarajevo (1986).
5. B.Repić, Lj.Jovanović, A.Salnikov, Ž.Kostić:
Mogućnosti smanjenja NO_x emisije na energetskim postrojenjima, *Zbornik radova sa savetovanja "Ekološki problemi Beograda - stanje i mogućnosti njihovog rešavanja"*, Vol.I, pp.59-66, Beograd, 13-15 December 1990.
6. V.P.Glushko, L.V.Gurevich:
Termodinamičeskie svoystva individualnykh veshchestv, Izd. "Nauka", Moskva, T.1 (1978), T.2 (1979).
7. J.H.Pohl, S.L.Chen, M.P.Heap, D.W.Pershing:
Correlation of NO_x Emissions with Basic Physical and Chemical Characteristics of Coal, *Proceedings of the 1982 Joint Symposium on Stationary Combustion NO_x Control*, pp.36/1-36/30, Vol.2, EPRI CS - 3182 (1983).
8. S.Djekić, M.Milosavljević:
Uticaj osobina Kosovskog lignita i ložišnih uslova na emisiju azotnih oksida iz kotlovskih postrojenja TE "Kosovo B", *Zbornik radova sa IX Stručnog savetovanja o termoelektranama*, pp.569-590, ZJE, Novi Sad (1991).
9. V.Jeftić:
Emisija azotnih oksida u termoelektranama na području Beograda; *Zbornik radova sa savetovanja "Uticaj termoeenergetskih objekata u zoni Beograda na kvalitet vazduha"*, I, pp.11/61-11/72, EPS, Beograd (1991).