

MODELING OF NITROGEN OXIDE RELEASE IN COAL COMBUSTION

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A model for and results of calculating the chemical-thermodynamic equilibrium of compounds and elements contained in coal and in the air required for combustion are presented. They can be used to evaluate the possibility of decreasing the NO_x release in the process of coal combustion.

Introduction. Fuel combustion is accompanied by a considerable amount of dust-laden gas release whose composition contains nitrogen oxides NO_x. The content of nitrogen oxides in flue gases is mainly decreased by two methods: cleaning the flue gases and controlling the process of combustion, the second method being used more frequently. To find a more convenient possibility of controlling the process of combustion, analysis of the effect of temperature on NO_x formation is required. It can be performed by a chemical-thermodynamic calculation of the equilibrium composition of the combustion products as a function of the combustion temperature.

Three mechanisms of formation of nitrogen oxides are known: 1) oxidation of molecular nitrogen of the air, 2) oxidation of nitrogen of the fuel, 3) formation of "fast" NO_x in the reaction of the fuel with molecular nitrogen. The "fast" oxides are usually disregarded in practice because of their small fraction. Depending on the nitrogen content the fraction of "fuel" nitrogen oxides amounts to 35–20% of the total release of NO_x in combustion of pulverized coal. In coals with a low nitrogen content (under 0.7%), the "thermal" mechanism of NO_x formation by oxidation of molecular nitrogen is predominant, the reaction rate depending strongly on the temperature. Measurements performed on a heat and power station that uses Kosovo lignite with a low nitrogen content showed that the "thermal" mechanism dominated even at low temperatures.

Thermodynamic calculations of the chemical equilibrium make it possible to isolate a narrow region of experimental investigations and to evaluate the probability of the occurrence of certain reactions. The equations employed for modeling the chemical-thermodynamic equilibrium of the system can be formulated using two basic approaches. One of them is based on the first variational principle of chemical thermodynamics, according to which in equilibrium states of the system the thermodynamic potentials take extremum values [1]. The second approach is based on the law of mass action (the method of equilibrium constants) [2, 3]. The two approaches are equivalent since the equilibrium constants of the chemical reactions at a constant total pressure are determined by the free enthalpies (the Gibbs energies) of the reagents and the combustion products [4].

Computational Method. Selection of the number of gaseous and condensed (solid and liquid) chemical components considered is the first step in modeling the chemical-thermodynamic equilibrium. If this number is m , including f condensed components, and q is the number of the chemical elements that form the system, there are $m - q$ equations of the law of mass action that govern the equilibrium composition of the system. In other words, there are $m - q$ independent equilibrium constants in the system. Usually, they are used for the reactions of decomposition of compounds into component atoms so that all the equations are independent and are calculated as

$$K_j = \prod_{i=1}^q p_i^{a_{ij}} / p_j, \quad j = 1, 2, 3, \dots, m - q. \quad (1)$$

In the case of condensed substances that do not form solid solutions, use of the law of mass action (since the partial saturation pressure over the condensed phase is constant at constant temperature) yields an additional f equations in the form

$$K_k^0 = p_k, \quad k = 1, 2, \dots, f. \quad (2)$$

For an ideal gaseous mixture, we also include Dalton's law in the system of thermodynamic-equilibrium equations:

$$\sum_{i=1}^m p_i = p. \quad (3)$$

To close the system of equations, we introduce $q - 1$ more equations of material balance

$$\frac{\sum_{i=1}^m a_{bi} p_i + \sum_{k=1}^f a_{bk} p v_k}{\sum_{i=1}^m a_{di} p_i + \sum_{k=1}^f a_{dk} p v_k} = \frac{B}{D}. \quad (4)$$

Mass-balance equation (4) points to the fact that one mole of any substance, in either the gaseous phase or the condensed phase, contains a number of molecules (atoms) equal to Avogadro's number.

The method of calculating the equilibrium constants in (1) using the change in the Gibbs energy, the coefficients of the polynomial that describes the modified Gibbs energy as a function of the temperature

$$\Phi(T) = -\frac{G(T) - H(T=0)}{T} = S(T) - \frac{H(T) - H(T=0)}{T},$$

and the enthalpy change in the chemical reactions of decomposition into atoms is given in [4, 5].

The system of nonlinear algebraic equations (1)-(4) has only one positive real solution for a specific reacting mixture [6] and is usually solved by the iteration method [2, 7].

Only the gaseous phase is considered below. In cases where the condensed phase is also taken into account, the constants of the vapor pressure over the condensed phase of the given chemical compound at the temperature in question and the balance equations for the atoms in the system that appear in the condensed phase are included in the system of thermodynamic-equilibrium equations [3]. In systems with a condensed phase, whatever the method of solution used, problems of convergence can arise. A detailed description of the calculation used here is given in [3].

Computational Procedure. Based on the equations presented, we developed a corresponding program for computation of equilibrium products of combustion or gasification and determination of the thermodynamic parameters of the state of the components and the products of combustion: H, H₂, S₂, O₂, N₂, SO, SO₂, SO₃, NO, I_g, H₂O, HO₂, CO, CO₂, OH, CH₄, C₂H₂, H₂S, N₂O, and NO₂. The thermodynamic parameters of state are: the Gibbs function, entropy, enthalpy, and specific heat of the components; the molar weight, gas constant, Gibbs function, density, enthalpy, and entropy of the products; the heat capacity of the nonreacting mixture.

The initial data for the computation are:

- a) the molar and atomic weights of the components: M_{N_2} , M_{O_2} , M_{CO_2} , A_{Ar} , M_{air} , A_H , A_C , A_N , A_O , A_S , and M_{H_2O} (expressed in kmole) [8];
- b) data for the coal (elemental analysis of the fuel: the content of C, H, N, O, and S, % of the m.m.f.), the oxidizer (the quantity y of air required for combustion of 1 kg of moisture-free ash-free fuel, kg/kg), and the water vapor (the quantity z of moisture in 1 kg of fuel in the as-received condition, kg/kg);
- c) the heat of the reactions [4], which can have both positive and negative values depending on the type of reaction (exothermic or endothermic);

TABLE 1. Technical and Elemental Analysis of Different Coals (per working mass)

No. of system	Coal	Moisture content	Ash content	C	H	N	O	S	y, kg of air/kg of fuel	z, kg of moisture/kg of fuel	α
1	Kolubara	9.99	27.04	40.13	3.90	0.79	17.03	1.12	8.357	0.1586	1.0
2	Tamnava	2.60	30.48	45.17	3.74	0.94	16.51	0.56	8.647	0.0389	1.0
3	Soko	1.93	26.53	48.23	4.14	1.41	16.78	0.98	8.782	0.0270	1.0
4	Plevlya	2.50	26.13	45.49	3.73	0.96	19.91	1.28	7.993	0.0350	1.0
5	Bogovina	0.89	29.84	46.36	3.16	1.18	16.13	2.44	8.404	0.0128	1.0
6	Ibar	0.22	53.67	35.37	2.67	1.24	1.31	5.52	11.196	0.0048	1.0
7	Suvodol	7.55	22.03	48.01	3.98	1.48	14.67	2.28	9.015	0.1072	1.0
8	Kakan'	1.77	42.65	39.99	3.07	1.44	9.46	1.61	9.558	0.0319	1.0
9	Soko	1.93	26.53	48.23	4.14	1.41	16.78	0.98	10.977	0.0270	1.25

TABLE 2. Atomic Fractions in the Elemental Composition of the Combustion Products

No. of system	Coal	C	H	N	O	S	Inert gases	α
1	Kolubara	0.07234	0.10760	0.61566	0.19998	0.0007550	0.00367	1.0
2	Tamnava	0.07710	0.08185	0.64104	0.19584	0.0003575	0.00382	1.0
3	Soko	0.07607	0.08173	0.64361	0.19417	0.0005781	0.00383	1.0
4	Plevlya	0.07817	0.08197	0.63627	0.19897	0.0008226	0.00379	1.0
5	Bogovina	0.07989	0.06682	0.65151	0.19633	0.0015725	0.00388	1.0
6	Ibar	0.07106	0.06439	0.67377	0.18261	0.0041467	0.00401	1.0
7	Suvodol	0.07414	0.08863	0.63689	0.19523	0.0031167	0.00379	1.0
8	Kakan'	0.07584	0.07372	0.65458	0.19082	0.0011418	0.00390	1.0
9	Soko	0.07447	0.8001	0.63006	0.21114	0.0005659	0.00375	1.25

d) data for calculating the equilibrium constants that include the coefficients of the polynomial that describes the temperature dependence of the modified Gibbs function and the enthalpy change for the chemical reactions of decomposition into the component atoms. The polynomial coefficients are taken according to [4] while the enthalpy change is determined experimentally [4] and can have positive and negative values depending on the type of reaction (exothermic or endothermic).

Results of the Calculation. The calculation was performed for several kinds of coal whose elemental and technical composition is given in Table 1. Kolubara, Tamnava, Plevlya, and Suvodol coals are lignites, Soko, Bogovina, and Kakan' coals are brown coals, and Ibar coal falls into bituminous coals.

Table 1 also contains data on the amount of moisture and air-oxidizer for coefficients of excess air $\alpha = 1$ (the stoichiometric quantity of air) and $\alpha = 1.25$. The coefficient α is calculated for the quantity of air required for oxidation of coal, sulfur, and hydrogen to CO_2 , SO_2 , and H_2O .

Results of calculating the thermodynamic equilibrium for all the systems (Tables 1 and 2) are given in Figs. 1 and 2. Calculated contents of some gaseous components of the combustion products with a partial pressure of over $1 \cdot 10^{-19}$ bar are presented.

Figure 1 shows the results of calculating all the gaseous components of the combustion products for system No. 9 (Soko brown coal). From the diagrams, it can be seen that the releases of nitrogen oxides (NO , NO_2 , and N_2O) depend on the temperature of coal combustion and increase with it. Although experimental investigations show a decrease in the N_2O content as the temperature increases [9], the results of the calculation are logical since they include only the effect of thermal formation of nitrogen oxides NO_x . At the same time, all three mechanisms

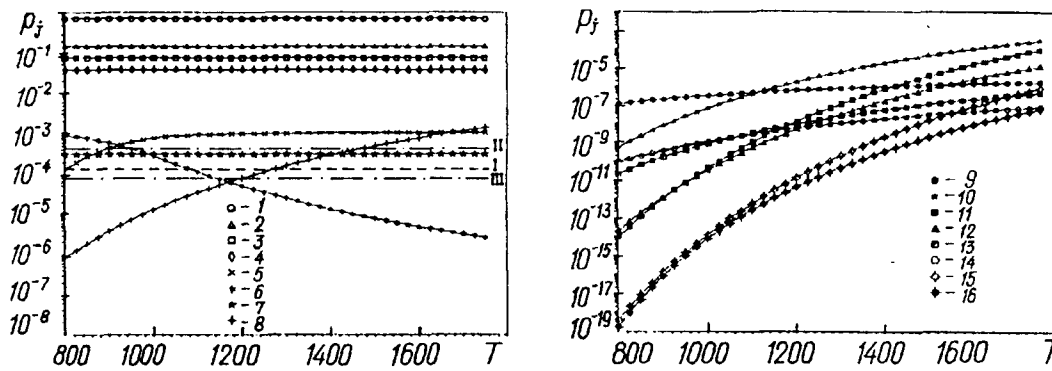


Fig. 1. Equilibrium composition of systems Nos. 1-8 (Table 1, $\alpha = 1.0$; No. 9, $\alpha = 1.25$): 1) N_2 , 2) CO_2 , 3) H_2O , 4) O_2 , 5) SO_2 , 6) SO_3 , 7) I_g , 8) NO , 9) NO_2 , 10) OH , 11) CO , 12) H_2 , 13) HO_2 , 14) N_2O , 15) H , 16) SO . p , bar; T , K.

of formation of nitrogen oxides NO_x meet the actual conditions of combustion. SO_2 releases depend mainly on the sulfur content in the coal being burned. The releases of SO_3 , conversely, are governed by the combustion temperature and decrease as it increases.

Among environmentally harmful gas releases, SO_2 and NO_2 and, at low temperatures of coal combustion, SO_3 are the most important. From Fig. 1, it can be seen that the contents of NO_2 and N_2O are negligibly small, and there are practically no other nitrogen oxides, i.e., their partial pressure is much below $1 \cdot 10^{-6}$ bar. However, even at these low concentrations (for example, at 1400 K, the concentration of N_2O is 0.037 mg/n. m^3 , which corresponds to a partial pressure of $0.18 \cdot 10^{-7}$ bar), the presence of N_2O is a great environmental hazard because of its high toxicity. Figure 1 shows the contents of SO_2 and NO_x that are limiting as far as the standard requirements are concerned [10]. Curve I denotes the limiting partial pressure of SO_2 ($0.14 \cdot 10^{-3}$ bar, which corresponds to a limiting concentration of SO_2 of 400 mg/n. m^3 for coals). Curve II shows the limiting partial pressure of NO_x for high-power boilers that have been in operation for a long time ($0.3896 \cdot 10^{-3}$ bar, which corresponds to a concentration of 390 ppm or $800 \text{ mg of } NO_2/\text{n. m}^3$) while curve III shows the limiting partial pressure of NO_x for new boilers ($0.9739 \cdot 10^{-4}$ bar, which corresponds to a concentration of 97.5 ppm or $200 \text{ mg of } NO_2/\text{n. m}^3$). From the diagram of Fig. 1 (for Soko brown coal for $\alpha = 1.25$), it can be seen that the NO_x content at a temperature of 1200 K exceeds the limiting value for new boilers and, at a temperature of 1400 K, it is greater than $800 \text{ mg of } NO_2/\text{n. m}^3$.

Figure 1 also shows results of measuring the amount of NO_x releases on 210-MW ($387 \text{ mg of } NO_2/\text{n. m}^3$, i.e., $0.189 \cdot 10^{-3}$ bar), 308-MW ($445 \text{ mg of } NO_2/\text{n. m}^3$, i.e., $0.21 \cdot 10^{-3}$ bar), and 620-MW ($653 \text{ mg of } NO_2/\text{n. m}^3$, i.e., $0.318 \cdot 10^{-3}$ bar) units at the "Nikola Tesla" heat and power plant and 32-MW ($406 \text{ mg of } NO_2/\text{n. m}^3$, i.e., $0.198 \cdot 10^{-3}$ bar) and 110-MW ($586 \text{ mg of } NO_2/\text{n. m}^3$, i.e., $0.285 \cdot 10^{-3}$ bar) units at the "Kolubara" heat and power plant, which burn pulverized Kolubara lignite. Average values of NO_x releases on these units are marked by the points.

Results of calculating the thermodynamic equilibrium in stoichiometric combustion ($\alpha = 1.0$) for system No. 3 (a similar calculation is also performed for Soko brown coal with a coefficient of excess air of under 1.0 for a constant partial pressure of O_2 of $1 \cdot 10^{-4}$ bar) showed that the NO_x releases can be decreased by providing stoichiometric conditions of combustion. This combustion method with small quantities of excess air is employed to decrease "fast" NO_x below the allowable level.

The methods for decreasing NO_x releases are surveyed in the literature [11]. Their essence consists in decreasing the temperature in zones of the boiler furnace in which it exceeds a certain value (for example, 1200 K, as in the case in Fig. 1) or in providing stoichiometric combustion in high-temperature zones.

Figure 2 gives results of calculations of NO , SO_2 , and SO_3 partial pressures for systems Nos. 1-8 (Table 1). They indicate that the partial pressures obtained for NO (Fig. 2a), NO_2 , and N_2O for all types of coals differ significantly: by approximately 40% for NO and NO_2 and by approximately 100% for N_2O). This points to high sensitivity of the developed model to the fuel characteristics.

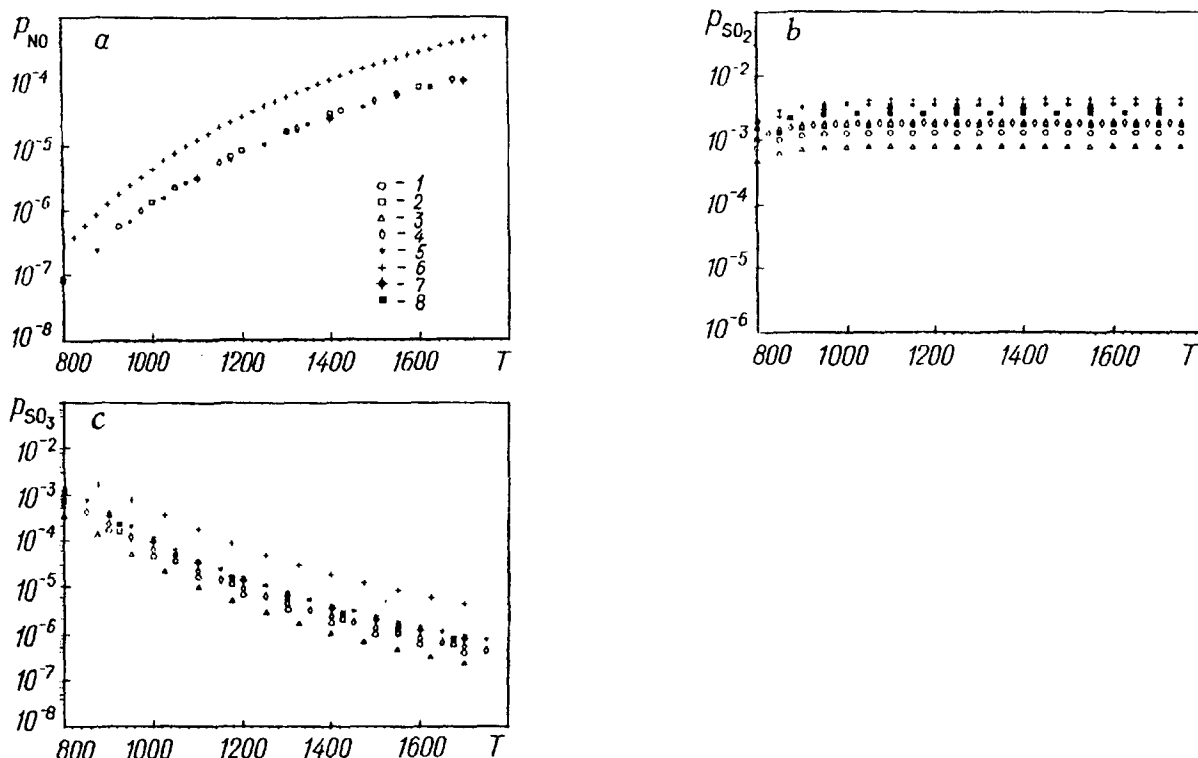


Fig. 2. Partial pressures of NO (a), SO₂ (b), and SO₃ (c) for systems Nos. 1-8 (Table 1, $\alpha = 1.0$): 1) Soko coal, 2) Kolubara, 3) Tamnava, 4) Plevlya, 5) Bogovina, 6) Ibar, 7) Suvodol, 8) Kakan'.

An analysis of the results in Figs. 1 and 2b shows that the volume of SO₂ release depends on the sulfur content in the fuel, the SO₂ concentration being practically independent of the temperature when it exceeds 900 K (for $\alpha = 1.0$). The calculated concentrations of SO₂ for different coals at the same temperature differ by more than a factor of 10. Calculated partial pressures of SO₃ are shown in Fig. 2. We can note that SO₃ release decreases with increasing temperature, i.e., SO₃ appears only at low temperatures. In addition to the temperature, the content of sulfur in the coal has a strong effect on SO₃ formation. Here, too, the calculated values for different coals differ by up to a factor of 10 at the same temperature.

Summary. In the work, we presented results of a calculation of the chemical-thermodynamic equilibrium for coal-air systems obtained using the mathematical model described. They show the effect of the composition of the coal and the coefficient of excess air on the formation of such components as H, H₂, S₂, O₂, N₂, SO, SO₂, SO₃, NO, Ig, H₂O, HO₂, CO, CO₂, OH, CH₄, C₂H₂, H₂S, N₂O, and NO₂ in the combustion products. The data obtained for several types of coal (lignite, brown coal, and bituminous coal) under different combustion conditions ($\alpha = 1.0$ and $\alpha = 1.25$) can be used to evaluate the possibility of decreasing the amount of NO_x releases by means of the corresponding organization of the process of combustion. Based on these data it is appropriate to eliminate high-temperature zones in furnaces in which NO_x formation exceeds the maximum allowable values. The equilibrium state of the system in the case of stoichiometric combustion is calculated and the possibility of decreasing the NO_x releases by means of combustion of the coal with a deficiency of the oxidizer is shown.

NOTATION

A , atomic weights; a_{ij} , stoichiometric coefficients in the decomposition reactions; a_{bi} , a_{di} , a_{bk} , and a_{dk} , number of atoms of the b and d types in the gaseous i and condensed k phases; B , total number of b -type atoms in the system; D , total number of d -type atoms in the system; f , number of condensed components; G , Gibbs energy (thermodynamic potential); H , enthalpy; Ig, inert gases; K_j , constants of the reactions of decomposition of complex components into atoms; k , atomic or molecular chemical component; m , number of gaseous and condensed (solid

and liquid) chemical components; M , molar weights; p_i , partial pressures of atomic elements; p_j , partial pressures of complex components; q , number of chemical elements; S , entropy; T , temperature; Φ , reduced Gibbs energy; y , quantity of air required for combustion of 1 kg of fuel; z , ratio of the quantity of moisture to 1 kg of fuel; α , coefficient of excess air; ν_k , ratio of the number of moles of substance k in the condensed phase to the total number of moles in the gaseous phase.

REFERENCES

1. W. B. White, S. M. Johnson, and G. B. Dantzig, *J. Chem. Phys.*, **28**, No. 5, 751 (1958).
2. A. L. Suris, *Thermodynamics of High-Temperature Processes: Handbook* [in Russian], Moscow (1985).
3. Ž. G. Kostić, P. Lj. Stefanović, and P. B. Pavlović, *Ceramics International*, **22**, No. 3, 179-186 (1996).
4. V. P. Glusko and L. V. Gurvich, *Thermodynamic Properties of Individual Substances* [in Russian], Moscow, Vol. 1 (1978); Vol. 2 (1979); Vol 3 (1981).
5. I. Glasman, *Combustion*, London (1987).
6. Ya. B. Zel'dovich, *Zh. Fiz. Khim.*, **2**, Issue 5, 685-689 (1938).
7. I. Glasman and R. F. Sawyer, *The Performance of Chemical Propellants*, Chapter II. Technivision, London (1970).
8. D. Kosić, B. Vasiliević, and V. Bekavats, *Handbook of Thermodynamics* [in Serbian], Belgrade (1986).
9. A. Braun, C. Bu, U. Renz, J. Drischel, and H. Koser, in: *ASME Fluidized Bed Combustion Conference*, Montreal (1991), pp. 709-717.
10. M. Krstić, *Technical Instructions for Maintenance of Air Purity* [in Serbian], Sarajevo (1986).
11. B. Repić, L. Yovanović, A. Sal'nikov, and Ž. Kostić, in: *Symposium "Environmental Problems of Belgrade,"* Belgrade (1991), Vol. 1, pp. 59-66.