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AN APPROXIMATE MODEL FOR THE GASES PROPAGATION WITH REACTION EMITTED FROM A THERMOELECTRIC PLANT - PART 2

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Abstract. *In the last decades, the propagation of chemical compounds in the atmosphere, coming mainly from human activities, has attracted attention. Faced with this, there is a compilation of emission factors for industrial sources. This is called "AP-42" - Compilation of Emission Factors of Atmospheric Pollutants. This work has developed a computer program that estimates the emission rates of the main compounds of a thermoelectric plant from the combustion of coal and the second part of the program carries out the propagation, dispersion and chemical reactions in the atmosphere. In this work the simplified chemical mechanism using only the chemistry of the Nitrogen gases (NO_x) is compared to a mechanism containing the chemistry of Nitrogen gases and the volatile organic compounds ("VOC"). Also shown is the solution method of the System of Coupled Ordinary Equations for the set of chemical reactions presented. The numerical results are presented for the concentrations of the gases Nitric Acid (HNO_3), Nitrogen Dioxide (NO_2), Nitric Oxide (NO) and Ozone (O_3).*

Keywords: *gases, propagation, chemical mechanism.*

1. INTRODUCTION

In the recent decades, air pollution has drawn attention because of their harmful effect on the environment. The study of the dispersion and transport of gases in the atmosphere has attracted the attention of many research groups. One of the sources of emissions is industrial smokestacks, Fenger (1999). These gases may undergo chemical transformations in the atmosphere to produce products that will interact with the environment. For example, Sulfur Oxides (SOx) and nitrogen (NOx) are precursors to acid rain and Nitrogen Dioxide (NO_2) gas produces ozone present in the lower atmosphere, Seinfeld and Pandis (2006). The spread of the gases emitted from a thermal power plant coal, is represented by an approximate model. The approximate model separates the propagation mechanism (advection and diffusion) and the chemical reaction. In this work the simplified chemical mechanism separating the chemistry of the Nitrogen gases (NOx) is compared to a mechanism containing the volatile organic compounds ("VOCs"). Also shown are the numerical results obtained for the concentrations of gases Nitric acid (HNO3), Nitrogen Dioxide (NO2), Nitrous oxide (NO) and Ozone (O3) generated from the emission source downwind.

2. APPROXIMATE MODEL OF SPREAD WITH CHEMICAL REACTION

2.1 Source Emission of the Coal Thermal Power Plant

The main gases involved with smog NOx, SOx, carbon monoxide (CO) and Volatile Organic Compounds (VOCs) have their flow rates estimated from emission factors inventory "AP-42", USEPA (1992). The flow rates of the gases leaving the chimney are estimated by the relation:

$$Q_{i,E} = A_i \times E_{F,i} \times (1 - \frac{E_{R,i}}{100}) \quad (1)$$

Where Q_i is the flow rate of the compound "i" (kg h-1) obtained by emission factors, A_i is the rate of fuel consumption (kg h-1), $E_{F,i}$ is the emission factor for gas " i "(kg gas" i "/ kg total) and $E_{R,i}$ is the elimination factor of the gas in the pollution removal equipment. The other gas flow rates are determined by stoichiometry ratios, the amount of excess air employed and elemental analysis of the Candiota Coal shown in Table 1, according to Rodrigues (2004). The amount of gas generated per each kg of coal from each element present in the coal, for example, carbon dioxide (CO_2) is obtained from the element Carbon (C) is obtained by the following equation

$$(X_{gi})_C = \frac{\bar{M}_{gi}}{\bar{M}_i}(X_i)_{um}) \quad (2)$$

Where $(X_{gi})_C$ is the amount of gas "gi" in kg per kg of coal, M_{gi} is the molar mass of the gas coming out the chimney and M_i is the molar mass of the element "i" that reacts with oxygen. The flow, the other gases, are given by the relation

$$Q_{i,D} = (X_{gi})_C A_i \quad (3)$$

Where $Q_{i,D}$ is the flow of other gases.

Table 1. Elementary data of the coal.

Compounds	% of the mass fraction
H_2O	3.58
Volatile material	19.77
Fixed Carbon	25.66
Ash	54.57
Sulfur	2.04
Carbon	32.26
Hydrogen	2.13
Nitrogen	0.67
Oxygen + halogen	8.33

2.2 The Propagation Model with Chemical Reaction

The propagation model (advection, dispersion and chemical reaction) of exhaust gases from the chimney adopts an instant release (so-called "puff") of rectangular shape, which separates the chemical reaction mechanisms and propagation at each liberation time of the "puff ", as Chiaramonte et al (2015). The chemical reaction model adopts the variation of the concentration of the gas mixture at a constant volume of the "puff", at each released time. And, the propagation model is an approximate model that applies to dilution of the total mass of gas released at the end of the travel time. The dilution model uses an analytical solution of the diffusion equation to evaluate the air intake at each displacement time.

3. MODELS OF CHEMICAL REACTIONS COMPARED

3,1 Simplified Mechanism of Nitrogen Compounds

In this work we adopted a simplified model for the evaluation of the nitric acid formed in the atmosphere from nitrogen compounds released in Thermal Power Plant. The set of reactions was uncoupled reactions of Volatile Organic Compounds (VOC) for an evaluation of the results and ease of solution of the set of ordinary differential equations that have numerical instability problem, as Yamartino et al. (1992). The set of reactions used is shown:

$$NO_2 + h\gamma \xrightarrow{O_2} NO + O_3 \qquad R_1 = J_1 C_{NO_2} \quad (4)$$

$$O_3 + h\gamma \rightarrow O_2 + O^* \qquad R_2 = J_2 C_{O_3} \tag{5}$$
$$O_3 + NO \rightarrow NO_2 + O_2 \qquad R_3 = k_3 C_{O_3} C_{NO} \tag{6}$$
$$H_2O + O^* \rightarrow 2OH \qquad R_4 = k_4 C_{H_2O} C_{O^*} \tag{7}$$
$$OH + NO_2 \rightarrow HNO_3 \qquad R_5 = k_5 C_{OH} C_{NO_2} \tag{8}$$

Where R_j is the rate of the reaction "j", J_j is the constant of the reaction photochemical "j", kj is the constant of the reaction "j", and C_i is the concentration of the compound "i".

The mechanism results in the system of coupled ordinary differential equations:

$$\frac{dC_{NO_2}}{dt} = -R_1 + R_3 - R_5 \tag{9}$$
$$\frac{dC_{NO}}{dt} = R_1 - R_3 \tag{10}$$
$$\frac{dC_{O_3}}{dt} = R_1 - R_2 - R_3 \tag{11}$$
$$\frac{dC_{o^*}}{dt} = R_2 - R_4 \tag{12}$$
$$\frac{dC_{H_2O}}{dt} = -R_4 \tag{13}$$
$$\frac{dC_{OH}}{dt} = 2R_4 - R_5 \tag{14}$$
$$\frac{dC_{HNO_3}}{dt} = R_5 \tag{15}$$

Where t is the release time of the gases in the source.

3.2 Mechanism of Nitrogen Compounds and Volatile Organic Compounds

A chemical mechanism by adding the compounds Carbon Monoxide (CO), Methane (CH4) and Sulfur compounds (SOx) to the chemistry of the Nitrogen compounds was implemented at this stage of the work. The set of reactions and the respective rates are shown in Equations (4) to (26):

The chemistry of Nitrogen compounds (NO_x):

$$NO_2 + h\gamma \xrightarrow{O_2} NO + O_3 \qquad R_1 = J_1 C_{NO_2} \tag{4}$$
$$O_3 + h\gamma \rightarrow O_2 + O^* \qquad R_2 = J_2 C_{O_3} \tag{5}$$
$$O_3 + NO \rightarrow NO_2 + O_2 \qquad R_3 = k_3 C_{O_3} C_{NO} \tag{6}$$
$$H_2O + O^* \rightarrow 2OH \qquad R_4 = k_4 C_{H_2O} C_{O^*} \tag{7}$$
$$OH + NO_2 \rightarrow HNO_3 \qquad R_5 = k_5 C_{OH} C_{NO_2} \tag{8}$$

The chemistry of Carbon Monoxide (CO):

$$CO + OH\cdot + O_2 \rightarrow CO_2 + HO_2\cdot \qquad R_6 = k_6\, C_{CO}\, C_{OH} \tag{16}$$
$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot \qquad R_7 = k_7\, C_{HO_2}\, C_{NO} \tag{17}$$

The chemistry of Methane (CH_4):

$$CH_4 + OH\cdot \rightarrow CH_3O_2\cdot + H_2O \qquad R_8 = k_8\, C_{CH_4}\, C_{OH} \tag{18}$$
$$CH_3O_2\cdot + NO + O_2 \rightarrow HCHO + HO_2\cdot + NO_2 \qquad R_9 = k_9 C_{CH_3O_2}.C_{NO} \tag{19}$$
$$CH_3O_2\cdot + HO_2\cdot \rightarrow CH_3OOH + O_2 \qquad R_{10} = k_{10} C_{CH_3O_2}.C_{HO_2}. \tag{20}$$
$$CH_3OOH + h\gamma + O_2 \rightarrow HCHO + HO_2\cdot + OH\cdot \qquad R_{11} = J_{11} C_{CH_3OOH} \tag{21}$$
$$CH_3OOH + OH\cdot \rightarrow H_2O + CH_3O_2\cdot \qquad R_{12} = k_{12}\, C_{C_{CH_3OOH}}\, C_{OH}. \tag{22}$$
$$CH_3OOH + OH\cdot \rightarrow H_2O + HCHO + OH\cdot \qquad R_{13} = k_{13}\, C_{C_{CH_3OOH}}\, C_{OH}. \tag{23}$$
$$HCHO + h\gamma + O_2 \rightarrow 2HO_2\cdot + CO \qquad R_{14} = J_{14}\, C_{HCHO} \tag{24}$$
$$HCHO + OH\cdot + O_2 \rightarrow HO_2\cdot + CO + H_2O \qquad R_{15} = k_{15}\, C_{HCHO}\, C_{OH}. \tag{25}$$
$$HO_2\cdot + O_3 \rightarrow OH\cdot + 2O_2 \qquad R_{16} = k_{16}\, C_{HO_2}.\, C_{O_3} \tag{26}$$
$$OH\cdot + O_3 \rightarrow HO_2\cdot + O_2 \qquad R_{17} = k_{17}\, C_{OH}.\, C_{O_3} \tag{27}$$
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad R_{18} = k_{18}\, C_{HO_2}.\, C_{HO_2}. \tag{28}$$
$$H_2O_2 + h\gamma \rightarrow 2OH\cdot \qquad R_{19} = J_{19}\, C_{H_2O_2} \tag{29}$$
$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \qquad R_{20} = k_{20}\, C_{H_2O_2}\, C_{OH}. \tag{30}$$

The chemistry of sulfur compounds (SO_x):

$$SO_2 + OH\cdot \rightarrow OHSO_2\cdot \qquad R_{21} = k_{21}\, C_{SO_2}\, C_{OH\cdot} \tag{31}$$

$$OHSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3 \qquad R_{22} = k_{22}\, C_{OHSO_2\cdot}\, C_{O_2} \tag{32}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad R_{23} = k_{23}\, C_{SO_3\cdot}\, C_{H2O_2} \tag{33}$$

This set of reactions origins the following set of ordinary differential equations that describe the mass balance in a system of constant volume for gases,

$$\frac{dC_{NO_2}}{dt} = -R_1 + R_3 - R_5 + \mathrm{R}_7 + \mathrm{R}_9 \tag{34}$$

$$\frac{dC_{NO}}{dt} = R_1 - R_3 - \mathrm{R}_7 - \mathrm{R}_9 \tag{35}$$

$$\frac{dC_{O_3}}{dt} = R_1 - R_2 - R_3 - R_{16} - R_{17} \tag{36}$$

$$\frac{dC_{o^*}}{dt} = R_2 - R_4 \tag{37}$$

$$\frac{dC_{H_2O}}{dt} = -R_4 + \mathrm{R}_8 + \mathrm{R}_{12} - R_{23} \tag{38}$$

$$\frac{dC_{OH}}{dt} = 2R_4 - R_5 - R_6 + R_7 - R_8 + R_{11} - R_{12} - R_{15} + R_{16} - R_{17} + 2R_{19} - R_{20} - R_{21} \tag{39}$$

$$\frac{dC_{HNO_3}}{dt} = R_5 \tag{40}$$

$$\frac{dC_{CO}}{dt} = -R_6 + R_{14} + R_{15} \tag{41}$$

$$\frac{dC_{CO_2}}{dt} = R_6 \tag{42}$$

$$\frac{dC_{HO_2}}{dt} = R_6 - R_7 + R_9 - R_{10} + R_{11} + 2R_{14} + R_{15} - R_{16} + R_{17} - 2R_{18} + R_{20} \tag{43}$$

$$\frac{dC_{CH_4}}{dt} = -R_8 \tag{44}$$

$$\frac{dC_{CH_3O_2}}{dt} = R_8 - R_9 - R_{10} + R_{12} \tag{45}$$

$$\frac{dC_{HCHO}}{dt} = R_9 + R_{11} + R_{13} - R_{14} - R_{15} \tag{46}$$

$$\frac{dC_{CH_3OOH}}{dt} = R_{10} - R_{11} - R_{12} - R_{13} \tag{47}$$

$$\frac{dC_{H_2O_2}}{dt} = R_{18} - R_{19} - R_{20} \tag{48}$$

$$\frac{dC_{SO_2}}{dt} = -R_{21} \tag{49}$$

$$\frac{dC_{HOSO_2}}{dt} = R_{21} - R_{22} \tag{50}$$

$$\frac{dC_{SO_3}}{dt} = R_{22} - R_{23} \tag{51}$$

$$\frac{dC_{H_2SO_4}}{dt} = R_{23} \tag{52}$$

The differential equations coupled system describe mass balance of the components of the chemical mechanism of the NOx, SOx, CH_4 and CO in a constant volume. The chemical reactions are treated independent of atmospheric dispersion (the procedure of dilution with atmospheric air). The system is solved at each "puff" displacement time by the method implicit numerical integration "Backward Differentiation Formula" fourth order BDF

$$y_n = \frac{48}{25}y_{n-1} - \frac{36}{25}y_{n-2} + \frac{16}{25}y_{n-3} - \frac{3}{25}y_{n-4} + h\frac{12}{25}f(y_n, t_n) \tag{53}$$

Where y_n is the value of the function at time "t_n", h is the integration step number f (y_n, t_n) is the derivative function of y calculated at the present time. The integration step is a very small value due to the problems of rigidity, the difference of reaction rates of the components, faster reactions and slow reactions. The discretization generates a non-linear system of equations for the concentrations. It is solved by the method of successive substitution at every step of integration.

4. METHODOLOGY

The methodology used was to apply the described model. It was implemented in a computer program in Fortran language, with the free software Force plus Fortran 90. The program makes the character data readings of the coal, the emission source, the composition of the atmosphere and the meteorological characteristics of the wind and performs the propagation model with chemical reaction.

5. RESULTS OBTAINED FROM THE MODEL

The model was used for an emission source, according to the data cited by the company (CGTEE, 2012) for the so-called "B" phase, for a sunny day with unstable atmosphere characteristics. These data are shown in Table 2. The results are shown in the graphs of Figures 1 and 2 which show the comparison of the simplified mechanism and the addition of the volatile compounds. The graphs show the concentration values, on the axis of the ordinates, against the distance of the point of emission, on the axis of the abscissa.

Table 2. Parameters used in the simulation.

Source emission data	
Flow rate, in kg s^{-1}	0.275560
chimney height, in m	150.0
Chimney diameter, in m	5.0
Atmosphere data	
Atmospheric pressure, in atm	1.0
Temperature, in ^{o}C	25.0
Air relative humidity, in %	30.0
Wind speed at 10 m, in m s^{-1}	7.0
Convective velocity, in m s^{-1}	1.64
Convective boundary layer length, in m	780.0

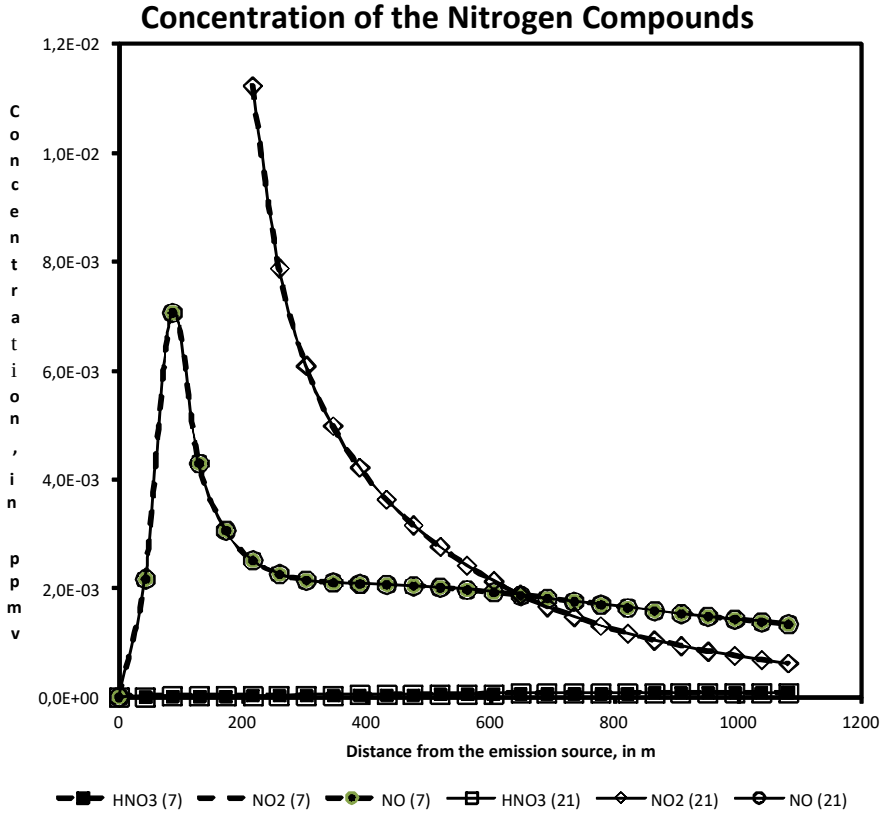

Figure 1. Concentration profile of Nitrogen compounds.

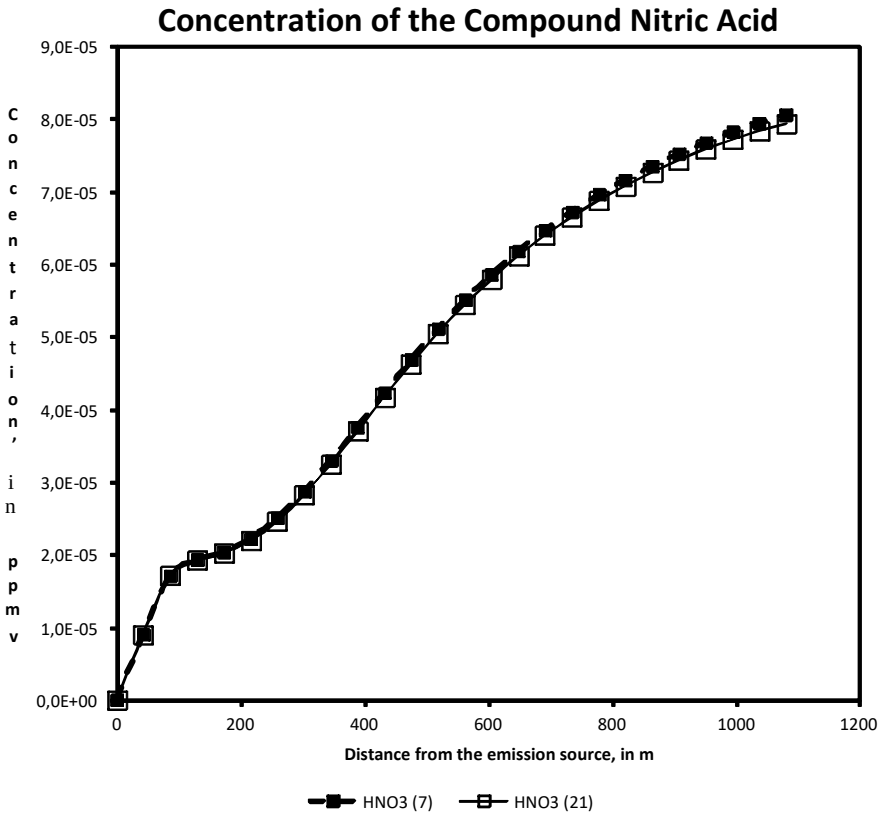

Figure 2. Concentration profile of the compound Nitric Acid.

6. CONCLUSIONS

This model approximate separating the dispersion mechanisms and overall chemical reaction is adequate because the solution becomes faster. The model will be developed further and more applications are performed.

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