VI International Conference on Computational Methods for Coupled Problems in Science and Engineering
COUPLED PROBLEMS 2015
B. Schrefler, E. Oñate and M. Papadrakakis (Eds)

MATHEMATICAL MODELING OF REACTION MECHANISM OF FORMATION OF PHOTOCHEMICAL SMOG BY APPLYING THE SEMI-IMPLICIT METHOD

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Key words: Rigid System, Jacobean, Formaldehyde, Photochemical Smog.

Abstract. To simulate the different mechanisms we considered a reactor of constant temperature and volume, where the only reactions that are carried out are those with reported kinetic constants [1]. For example, to simulate the formaldehyde kinetic you make a serial of seven chemical reactions where intervene nine chemical species [2].The change in concentration with respect to the time of one specie is mathematically represented by means of an ordinary differential equation. In the studied cases, the mechanism of reaction can be represented as a system of nonlinear ordinary differential equations. In the simulation of the mechanism of reaction, the medullar part is the solution of all the ordinary differential equation that describe the temporary evolution of the concentration of each the species. The differential equation that comes from the kinetic present what it is called rigidity, principally due to the simultaneous presence of radical with called rigidity, principally due to the simultaneous presence of radicals with a really short life time as the presence of hydroperoxide HO_2• and species that remain almost constant as the oxygen. The main problem to carry out the precise integration of the differential equation system that represents the mechanism of reaction of the atmospheric chemistry, is the wide when variation of the kinetic constant as it appears in the reactions 2 and 7 which brings as a consequence the instability when applying an explicit numerical method because for any change in so different scales. When this happens, it is said that the differential equation system is rigid. In order to solve the problem that the rigidity of a differential equation system represented we should use special numerical method that ensures precision and stability in its integration. To achieve this whit a classical explicit method it is required a lot of computing time, besides the possible instability. When using the semi implicit method, we developed a computer package using language C++ to solve the system of nonlinear ordinary differential equation. Solving the matrix system with the method mentioned above, it is found the numerical value of the concentration of the five chemical species for every time step, given the initial concentration. The computer program used to solve the system of

differential equation was developed in UNAM.

1 INTRODUCTION

All The core part in mathematical simulation of reaction mechanism of volatile organic compounds contained in highly polluted atmospheres, it is the solution of the set of ordinary differential equations describing the time evolution of the concentration of the chemical species. [1] The differential equations that result from chemical kinetics feature called rigidity, mainly due to the simultaneous presence of radical free with life time very short and of species that remain nearly constant as it is the content of oxygen, carbon dioxide and nitrogen.

Proposed mechanisms of photochemical smog formation reaction by different organic compounds, it was to make the computer simulation of the chemical kinetics from different initial conditions, in order to see the change of the concentrations of each species at the time.

To perform the mathematical simulation [2] of the different mechanisms is considered a reactor volume and temperature constant, where only carry out reactions indicated for each mechanism.

The change of concentration with focus in the time of a sort it is represented mathematically by means of an ordinary differential equation. In the cases studied, the reaction mechanism can be represented as a system of nonlinear ordinary differential equations, in the following steps:

$$\frac{dC_1}{dt} = f_1(C_1 \ldots\ldots\ldots C_n)$$

$$\frac{dC_2}{dt} = f_2(C_1 \ldots\ldots\ldots C_n)$$

•

•

•

$$\frac{dCn}{dt} = f_n(C_1 \ldots\ldots\ldots C_n)$$

Where C_1, $C_2 \ldots C_n$ represent the concentrations of each of the n chemical species.

This type of system is known as autonomous, due to the independent variable time does not appear explicitly in the functions $f_1, f_2, \ldots, f_n$.

The main problem to realize the integration of systems of differential equations that represent of atmospheric chemistry reaction mechanisms, it is the wide variation of the kinetic constants, which brings as consequence the instability by applying an explicit numerical method as for a change in the independent variable, the dependent variables change at very different scales. When this happens, it is said that the system of differential equations is a rigid system.

The matrix $\boldsymbol{J}$, which contains the partial derivatives of functions $\boldsymbol{f_i}$, with respect to each of the chemical species, concentration plays an important role in the application of numerical methods to rigid systems. The determinant of the matrix $\boldsymbol{J}$ is known as Jacobean. The rigid system is characterized when the matrix $\boldsymbol{J}$ has widely disparate characteristic values.

More stringent, a rigid system occurs when:

• The real parts of the eigenvalues of the matrix ***J*** is less than zero.

• The quotient that results from dividing the real part of the maximum characteristic value, between the real parts of the smallest characteristic value is much greater than one.

A special numerical method that ensures accuracy and stability in their integration should be used to solve the problem that represents the rigidity of a system of differential equations. Long time is required to achieve this with an explicit classical method, computer, apart from the possible instability.

This work used the semi-implicit method, which allows to solve the above mentioned problem.

If we consider as an example the following differential equations with their respective initial conditions:

$$y' = f_1(x, y, z);\ y(x_0) = y_0$$
$$z' = f_2(x, y, z);\ z(x_0) = z_0$$

It is denoted as u the numerical value of y as the numerical value of z v, then using the semi-implicit method, differential equations are represented in the following way:

$$\frac{u_{n+1} - u_n}{h} = \frac{1}{2}[f_1(x_{n+1}, u_{n+1}, v_{n+1}) + f_1(x_n, u_n, v_n)]$$
$$\frac{v_{n+1} - v_n}{h} = \frac{1}{2}[f_2(x_{n+1}, u_{n+1}, v_{n+1}) + f_2(x_n, u_n, v_n)]$$

Where u_0 and v_0 is the initial condition y_0 and z_0.

Applying the formula of Taylor to functions on the right side, are the following linear equations with respect to u_{n+1} and v_{n+1}:

$$u_{n+1} - u_n = \frac{h}{2}[f_1(B) + (u_{n+1} - u_n)\frac{\partial f_1(B)}{\partial y} + (v_{n+1} - v_n)\frac{\partial f_1(B)}{\partial z} + \ldots + f_1(I)]$$
$$v_{n+1} - v_n = \frac{h}{2}[f_2(B) + (u_{n+1} - u_n)\frac{\partial f_2(B)}{\partial y} + (v_{n+1} - v_n)\frac{\partial f_2(B)}{\partial z} + \ldots + f_2(I)]$$

where B is (x_{n+1}, u_n, v_n) e $I\ (x_n, u_n, v_n)$.

If defined:

$$u^* = u_{n+1} - u_n$$

Then:

$$u^* = \frac{h}{2}f_1(B) + \frac{h}{2}u^*\frac{\partial f_1(B)}{\partial y} + \frac{h}{2}v^*\frac{\partial f_1(B)}{\partial z} + \frac{h}{2}f_1(I)$$
$$v^* = \frac{h}{2}f_2(B) + \frac{h}{2}u^*\frac{\partial f_2(B)}{\partial y} + \frac{h}{2}v^*\frac{\partial f_2(B)}{\partial z} + \frac{h}{2}f_2(I)$$

Fixing these equations in matrix form, it is:

$$\begin{pmatrix} u^* \\ v^* \end{pmatrix} = \begin{pmatrix} \frac{h}{2}f_1(B) \\ \frac{h}{2}f_2(B) \end{pmatrix} + \begin{pmatrix} \frac{h}{2}f_1(I) \\ \frac{h}{2}f_2(I) \end{pmatrix} + \begin{pmatrix} \frac{h}{2}\frac{\partial f_1(B)}{\partial y} & \frac{h}{2}\frac{\partial f_1(B)}{\partial z} \\ \frac{h}{2}\frac{\partial f_2(B)}{\partial y} & \frac{h}{2}\frac{\partial f_2(B)}{\partial z} \end{pmatrix}\begin{pmatrix} u^* \\ v^* \end{pmatrix}$$

Then:

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} u^* \\ v^* \end{pmatrix} - \begin{pmatrix} \frac{h}{2}\frac{\partial f_1(B)}{\partial y} & \frac{h}{2}\frac{\partial f_1(B)}{\partial z} \\ \frac{h}{2}\frac{\partial f_2(B)}{\partial y} & \frac{h}{2}\frac{\partial f_2(B)}{\partial z} \end{pmatrix}\begin{pmatrix} u^* \\ v^* \end{pmatrix} = \begin{pmatrix} \frac{h}{2}f_1(B) + \frac{h}{2}f_1(I) \\ \frac{h}{2}f_2(B) + \frac{h}{2}f_2(I) \end{pmatrix}$$

Therefore:

$$\begin{pmatrix} 1 - \frac{h}{2}\frac{\partial f_1(B)}{\partial y} & -\frac{h}{2}\frac{\partial f_1(B)}{\partial z} \\ -\frac{h}{2}\frac{\partial f_2(B)}{\partial y} & 1 - \frac{h}{2}\frac{\partial f_2(B)}{\partial z} \end{pmatrix}\begin{pmatrix} u^* \\ v^* \end{pmatrix} = \begin{pmatrix} \frac{h}{2}f_1(B) + \frac{h}{2}f_1(I) \\ \frac{h}{2}f_2(B) + \frac{h}{2}f_2(I) \end{pmatrix}$$

Solving this system of two simultaneous linear equations are the values of u^* and v^*, and therefore the values of $v_{n+1}.1$ and v_{n+1}.

To use the semi-implicit method a computer package in c++ was developed to solve systems of nonlinear ordinary differential equations.

2 REACTION MECHANISM

To illustrate the method used semi-implicit and simulate the chemical kinetics of the reaction mechanism proposed mathematical modeling of formaldehyde (HCHO) considered is shown as you pollute the main secondary highly polluted atmospheres.

In this case indicates the mechanism of reaction of formaldehyde [3,4] where it can react with in the presence of light or the hydroxyl radical release hydro peroxide, carbon monoxide and water respectively.

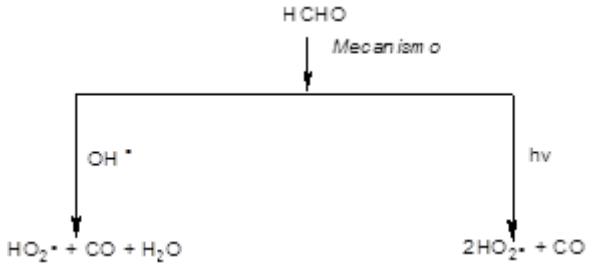

Figure 1. Mechanism of reaction of formaldehyde.

In the proposal chemical kinetics are considered chain reactions, as initial reactions of the cycle [5] basic photochemical smog, indicated in the following three first reactions and their respective kinetic constants.

$NO_2 + h\gamma \longrightarrow NO + O$	$k_1=0.533$
$O + O_2 + M \longrightarrow O_3 + M$	$k_2=2.183X10^{-5}$
$NO + O_3 \longrightarrow NO_2 + O_2$	$k_3=26.59$

Propagation reactions correspond to reaction mechanism shown above in Figure 1.

$HCHO + h\gamma \xrightarrow{2O_2} 2HO_2^{\bullet} + CO$ $\quad k_4=2.35x10^{-3}$

$HCHO + HO^{\bullet} \xrightarrow{O_2} HO_2^{\bullet} + CO + H_2O$ $\quad k_5=1.6x10^{4}$

And the corresponding termination reactions of the hydroxyl and hydro peroxide to form nitrogen dioxide and nitric acid respectively.

$HO_2^{\bullet} + NO \longrightarrow {}^{\bullet}OH + NO_2$ $\quad k_6=1.214x10^{4}$

${}^{\bullet}OH + NO_2 \longrightarrow HNO_3$ $\quad k_7=I.613x10^{4}$

The different chemical species formed are the following nine: C_1=NO, C_2=NO_2, C_3=O_3, C_4=O, C_5=HCHO, C_6=${}^{\bullet}$OH, C_7=$HO_2^{\bullet}$, C_8=HNO_3 y C_9=CO.

3 MATHEMATICAL SIMULATION

The change of concentration of chemical species focus in the time it is given by the following functions or differential equations:

```
f_r[1]:=k1*c[2]-k3*c[1]*c[3]-k6*c[1]*c[7];
f_r[2]:=-k1*c[2]+k3*c[3]*c[1]+k6*c[1]*c[7]-k7*c[2]*c[6];
f_r[3]:=k2*c[4]*C_O2*C_M-k3*c[3]*c[1];
f_r[4]:=k1*c[2]-k2*c[4]*C_O2*C_M;
f_r[5]:=-k4*c[5]-k5*c[5]*c[6];
f_r[6]:=-k5*c[5]*c[6]+k6*c[1]*c[7]-k7*c[2]*c[6];
f_r[7]:=2*k4*c[5]+k5*c[5]*c[6]-k6*c[1]*c[7];
f_r[8]:=k7*c[2]*c[6];
f_r[9]:=k4*c[5]+k5*c[5]*c[6];
```

While the partial derivatives with the concentration of each of the nine species in each of the seven reactions and chemical, it is given by the set of the following equations

```
Df_Dy[1,1]:=-k3*c[3]-k6*c[7];
Df_Dy[1,2]:=k1;
Df_Dy[1,3]:=-k3*c[1];
Df_Dy[1,7]:=-k6*c[1];

Df_Dy[2,1]:=k3*c[3]+k6*c[7];
Df_Dy[2,2]:=-k1-k7*c[6];
Df_Dy[2,3]:=k3*c[1];
Df_Dy[2,6]:=-k7*c[2];
Df_Dy[2,7]:=k6*c[1];

Df_Dy[3,1]:=-k3*c[3];
Df_Dy[3,3]:=-k3*c[1];
Df_Dy[3,4]:=k2*C_O2*C_M;
```

```
Df_Dy[4,2]:=k1;
Df_Dy[4,4]:=-k2*C_O2*C_M;

Df_Dy[5,5]:=-k4-k5*c[6];
Df_Dy[5,6]:=-k5*c[5];

Df_Dy[6,1]:=k6*c[7];
Df_Dy[6,2]:=-k7*c[6];
Df_Dy[6,5]:=-k5*c[6];
Df_Dy[6,6]:=-k5*c[5]-k7*c[2];
Df_Dy[6,7]:=k6*c[1];

Df_Dy[7,1]:=-k6*c[7];
Df_Dy[7,5]:=2*k4+k5*c[6];
Df_Dy[7,6]:=k5*c[5];
Df_Dy[7,7]:=-k6*c[1];

Df_Dy[8,2]:=k7*c[6];
Df_Dy[8,6]:=k7*c[2];

Df_Dy[9,5]:=k4+k5*c[6];
Df_Dy[9,6]:=k5*c[5];
```

Where is the matrix resulting Jacobean J as follows:

$-K_3C_3-K_6C_7$	K_1	$-K_3C_1$	0	0	0	$-K_6C_1$	0	0
$K_3C_3+K_6C_7$	$-K_1-K_7C_6$	K_3C_1	0	0	$-K_7C_2$	K_6C_1	0	0
$-K_3C_3$	0	$-K_3C_1$	$K_2CO_2C_M$	0	0	0	0	0
0	K1	0	$-K_2CO_2C_M$	0	0	0	0	0
0	0	0	0	$-K_4-K_5C_6$	$-K_5C_5$	0	0	0
K_6C_7	$-K_7C_6$	0	0	$-K_5C_6$	$-K_5C_5-K_7C_2$	K_6C_1	0	0
$-K_6C_7$	0	0	0	$2K_4+K_5C_6$	K_5C_5	$-K_6C_1$	0	0
0	K_7C_6	0	0	0	K_7C_2	0	0	0
0	0	0	0	$K_4+K_5C_6$	K_5C_5	0	0	0

Solving the matrix system by the above mentioned method, you will find the numerical value of the concentrations of nine chemical species for each step in time, given the initial concentrations, specifically set the more stable compounds.

The computer program used to solve the system of differential equations, developed in the Center of research theory of the Faculty of studies Cuautitlán of UNAM, includes:

• The routine implementation of the Semi-implicit method for rigid systems of coupled nonlinear ordinary differential equations.

• The routine of Gauss elimination method for solving systems of linear algebraic equations

simultaneous.

• Graphing of results written in c++.

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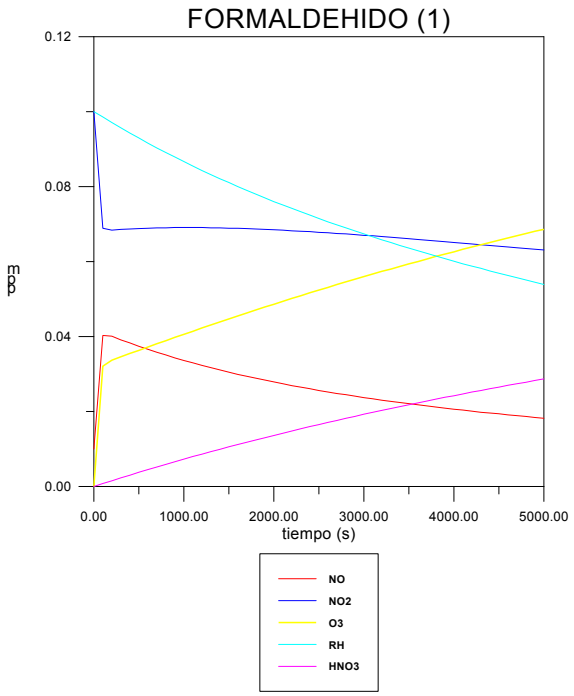
4. ANALYSIS OF RESULTS

In the first run of the program (case 1), were assigned as initial conditions NOx concentrations closer to the atmosphere highly contaminated, i.e. 0.1 ppm NO_2 which can be found in greater proportion due to the oxidizing conditions of the environment, and 0.01 ppm of NO. The concentration for each hydrocarbon depicted in graphs as RH, was 0.1ppm, taking into account that the emissions allowed by Mexican legislation in total hydrocarbons (NOM 041 ECOL 93) emission standards [6] for the cars of prior to 1979 are 700 ppm, and from 1994 to date, is 200 ppm, and that on average will emit 400 compounds in different proportions.

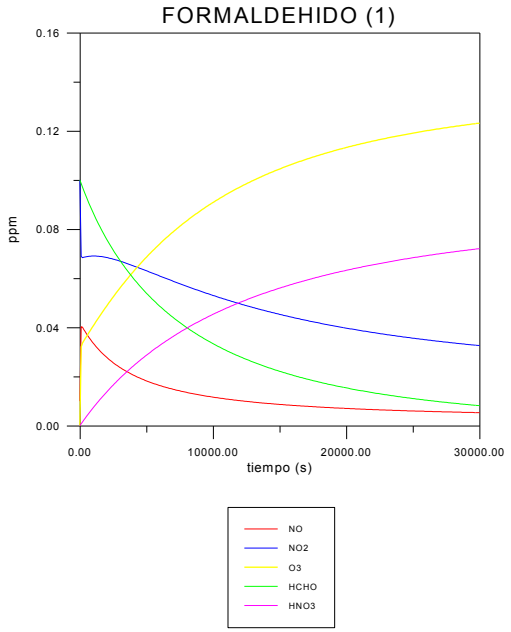
The time selected for the majority of cases was 5000 seconds, since during this time are observed changes in concentration of ozone and the emergence of other secondary pollutants, except in some cases where it is carried out only in the opening 100 seconds so it is 400 seconds, or in older times chart, as it is the case of acetone, which doubled the time.

Analyze the curves corresponding to the first run, you can see similar behavior in which the NO concentration increases, the NO_2 decreases and starts the formation of ozone reaching a maximum concentration of 0.072 ppm, while nitric acid reaches a concentration 0.0325 ppm, consumption of formaldehyde, the increase of the concentration of NO maximum to 0.0419 ppm and subsequent consumption, reduction of NO_2 to 0.0674 average ppm and subsequent production, formaldehyde is consumed rapidly, reducing its concentration to 0.059 ppm.



Graphic 1. Mathematical simulation of formaldehyde to 5000 seconds

The same initial conditions were considered in the second run (case 2) only change the response time with different times to observe the response of the program, managing to find that 30 000 seconds it is reached stability or equilibrium of reaction, reaching consume practically formaldehyde and not, to decrease to less than half the NO_2, ozone reaching concentrations de0.12 ppm and nitric acid of 0.0725 ppm.



Graphic 1. Mathematical simulation of formaldehyde to 30000 seconds

5 CONCLUSIONS

The proposed computational program responds to the solution of differential equations, derived partial and Jacobean of rigid systems, product of the mathematical simulation of chemical kinetics of volatile organic compounds in highly polluted atmospheres, this program can be applied to a myriad of possibilities [7] where you can change. The type of compound, the reaction mechanism, the concentration of the chemical species or reaction time.

In the event proposed for this presentation that was formaldehyde, chemically explains the high reactivity and justifies the high concentration of pollutants side such as ozone which is measured in different cities to evaluate air pollution and nitric acid which can produce acid rain.

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