NUMERICAL SIMULATION FOR REDUCED CHEMICAL KINETIC MECHANISM: A CASE FOR CARBON MONOXIDE AND HYDROGEN

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Abstract. *Stiff ODE systems are present in the most of chemical kinetic mechanisms and their numerical simulation has a very high computational cost. Because of this came the necessity to improve the employed work to solve this problems and choose an attractive method for numerical simulation with good accuracy and consistent results. Applying and validating the steady-state hypothesis for some chemical species, we build a reduced mechanism for carbon monoxide with three steps, contend as sub-mechanism the two-step reduced mechanism for hydrogen. For the numerical simulation, we have used the Rosenbrock method of the fourth order, for have the necessary stability and it leads to good results with low tolerance of error in comparison with other data found in the literature.*

Keywords: *Stiff ODE, Hydrogen, Carbon monoxide, Chemical kinetic mechanisms, Rosenbrock.*

1. INTRODUCTION

The high emission rates of pollutants have contributed significantly to the global warming, being necessary the research of new sources of energy. Hydrogen is considered a promising source of combustion for energy production. In (1) we note Hydrogen can be used in internal combustion engines and in fuel cells free of greenhouse gas emissions, when combusted with oxygen, water vapor being the only significant product. Other benefits can be highlighted with high energy yield (122 kJ / g), it is the most abundant element in the earth and that can also be produced through other primary sources of energy. One of the factors that prevents its frequent use is that it has low density, can not be found free in nature, low ignition energy, making it currently very expensive.

Researchs has also been done on other non-fossil fuel options such as ethanol, which has been gaining ground in the market and is a strong candidate to replace gasoline and can be obtained from vegetable sources such as sugarcane and corn . Research has been done on methanol that characterizes an important stage in the biodiesel chain and methane that is an important biogas species. All these systems have large size, many stages and a large number of chemical species. These mechanisms follow a hierarchical logic (7) and to accurately understand and manipulate their mixtures, it becomes necessary to study each step of the process. This is why the study of the carbon monoxide chain is fundamental, as well as the sub-mechanism of all these large systems, also involves the mechanism of combustion of hydrogen.

For the combustion of carbon monoxide are necessary twenty-six elementary reactions involving eleven chemical species. As a subsystem of monoxide, it is present the process of combustion of hydrogen, where are necessary twenty-one elementary reactions and ten chemical species, both presented by (4). They presented very reactive radicals, taking stiffness to the equations of production and consumption of each chemical species (2). A stiff ODE system has very different orders of magnitude, making the numerical resolution complex with a high computational cost, being essential the development of a reduced mechanism.

In this work, will be presented the combustion mechanism of carbon monoxide and hydrogen, a methodology for the calculus of each chemical species reaction rate and a strategy to reduce this mechanisms. Will be presented also a numerical simulation using Rosenbrock method.
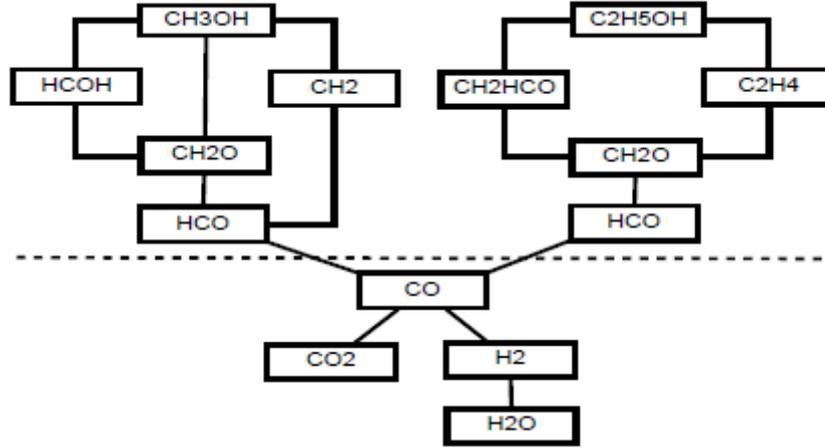
Figure 1. Hidrocarbonets chain presented by (2).

2. CARBON MONOXIDE AND HYDROGEN MECHANISMS

According with (5), the rate at which the reaction occurs is directly proportional to the concentration of the chemical species present in the reaction, so:

$$\frac{d[A]}{dt} = k(T)[A][B], \tag{1}$$

where k is a function of the temperature T and represents the specific rate of each reaction, being calculated by:

$$k = AT^{\beta} exp\left(-\frac{E_A}{RT}\right), \tag{2}$$

with A being a frequency factor, β the temperature exponent, E_A the activation energy and R the universal gas constant, all obtained empirically.

Considering the reactions $1-20$ (hydrogen-oxygen subset), $111-114$ (consumption of HCO) and 126 (consumption of CO) presented by (4), we have the skeletal mechanism for the carbon monoxide according to Table 1.
In the reaction where the species are produced, the plus sign is used, while in the reactions where the species are consumed, the minus sign is used. As an example, the rate of hydrogen will be:

$$\frac{d[H_2]}{dt} = - k_1[OH][H_2] + k_{1b}[H][H_2O] - k_3[O][H_2] + k_7[H][HO_2] \tag{3}$$
$$+ k_{11}[H]^2[M] + k_{17}[H_2O_2][H] + k_{114}[HCO][H].$$

Repeating this process for the other chemical species, we have a ODE system that can determine the concentration of the species at any time t. The values of k tend to present very different orders. This indicates that the ODE system is stiff and may have difficult to obtain a numerical solve.

The main idea of reducing mechanism applying asymptotic analysis is validate the steady-state hypothesis for species that are produced in very slow reactions and consumed is very fast reactions. Thus, the concentration remains low, not interfering in the combustion process.

Introducing the linear differential operator $W(Ci)$ and assuming the steady-state hypothesis for the species O, OH, HO_2 and HCO, they can be equal to zero. The resultant equation can be recombined, then the result will be a system with five algebraic equations.

$$w_6 = w_4 - w_5 - w_7 - w_8 - w_9 - w_{15} + w_{16} - w_{18} + w_{111}. \tag{4a}$$
$$w_{12} = - w_1 + w_{1b} - 2w_2 + 2w_4 - 3w_5 - 2w_7 - w_8 - 2w_9+ \tag{4b}$$
$$w_{10} - 2w_{14} - 3w_{15} - w_{16} + w_{17} + w_{19} + 2w_{111} - w_{126}. \tag{4c}$$
$$w_{13} = - w_2 + w_3 + w_8 - w_9 + w_{10} - 2w_{14} - w_{19}. \tag{4d}$$
$$w_{20} = w_{15} + w_{16} - w_{17} - w_{18} - w_{19}. \tag{4e}$$
$$w_{113} = - w_{111} - w_{112} - w_{114}. \tag{4f}$$

Table 1. Carbon monoxide mechanism rate coefficients (units are: mol, cm^3, s, K, and cal/mol).

Reaction	A	β	E_A
1. $OH + H_2 = H + H_2O$	$2.14E + 08$	1.52	3449
1b. $H + H_2O = OH + H_2$	$5.09E + 09$	1.3	18588
2. $O + OH = O_2 + H$	$2.02E + 14$	0.40	0.00
3. $O + H_2 = OH + H$	$5.06E + 04$	2.67	6290
4. $H + O_2 + M = HO_2 + M$	$4.52E + 13$	0.00	0.00
5. $OH + HO_2 = H_2O + O_2$	$2.13E + 28$	-4.83	3500
6. $H + HO_2 = OH + OH$	$1.50E + 14$	0.00	1000
7. $H + HO_2H = H_2 + O_2$	$6.63E + 13$	0.00	2126
8. $H + HO_2 = O + H_2O$	$3.01E + 13$	0.00	1721
9. $O + HO_2 = O_2 + OH$	$3.25E + 13$	0.00	0.00
10. $2OH = O + H_2O$	$3.57E + 04$	2.40	-2112
11. $H + H + M = H_2 + M$	$1.00E + 18$	-1.00	0.00
12. $H + OH + M = H_2O + M$	$2.21E + 22$	-2.00	0.00
13. $H + O + M = OH + M$	$4.71E + 18$	-1.00	0.00
14. $O + O + M = O_2 + M$	$1.89E + 13$	0.00	-1788
15. $HO_2 + HO_2 = H_2O_2 + O_2$	$4.20E + 14$	0.00	11982
16. $OH + OH + M = H_2O_2 + M$	$1.24E + 14$	-0.37	0.00
17. $H_2O_2 + H = HO_2 + H_2$	$1.98E + 06$	2.00	2435
18. $H_2O_2 + H = OH + H_2O$	$3.07E + 13$	0.00	4217
19. $H_2O_2 + O = OH + HO_2$	$9.55E + 06$	2.00	2435
20. $H_2O_2 + OH = H_2O + HO_2$	$2.40E + 00$	4.04	-2162
111. $HCO + O_2 = HO_2 + CO$	$7.58E + 12$	0.00	410
112. $HCO + M = H + CO + M$	$1.86E + 17$	-1.00	17000
113. $HCO + OH = H_2O + CO$	$1.00E + 14$	0.00	0.00
114. $HCO + H = CO + H_2$	$1.19E + 13$	0.25	0.00
126. $CO + OH = CO_2 + H$	$9.42E + 03$	2.25	-2351

These five equations can be simplified introducing the rates $W_{I'}$, $W_{II'}$ and $W_{III'}$:

$$W_{I'} = w_{126}. \tag{5a}$$

$$W_{II'} = -w_2 + w_4 - w_5 - w_7 - w_9 - w_{14} - w_{15} + w_{111}. \tag{5b}$$

$$W_{III'} = -w_1 + w_{1b} - 3w_2 - w_3 + 3w_4 - 3w_5 - 2w_7 - 3w_9 \tag{5c}$$

$$+ w_{11} - 3w_{14} - 3w_{15} + w_{17} + 3w_{111} + w_{114} - w_{126}. \tag{5d}$$

Making a linear combination, we have this rates for the resulting species:

$$W(C_{H_2}) = +w_{I'} - 3w_{II'} + w_{III'} \tag{6a}$$

$$W(C_H) = +2w_{II'} - 2w_{III'} \tag{6b}$$

$$W(C_{O_2}) = -w_{I'} \tag{6c}$$

$$W(C_{H_2O}) = -w_{I'} + 2w_{II'} \tag{6d}$$

$$W(C_{CO}) = -w_{I'} \tag{6e}$$

$$W(C_{CO_2}) = +w_{I'} \tag{6f}$$

The stoichiometry of these equations is equivalent to the three-step mechanism for the carbon monoxide (I, II, III), which includes the two-step mechanism for the hydrogen (II and III). Which is in accordance with the reduced mechanism found by (2).

$$I' \quad CO + H_2O = CO_2 + H_2. \tag{7a}$$

$$II' \quad 3H_2 + O_2 = 2H + 2H_2O. \tag{7b}$$

$$III' \quad H + H + M = H_2 + M. \tag{7c}$$

In this mechanism, the reaction I' represents the total consumption of CO, where there is no production or destruction of intermediate species. The reaction II' is the global reaction of the radicals produced and an oxygen consumption step and the reaction III' represents an overall recombination step with M being a catalyst.

3. NUMERICAL RESULTS

In order to simulate the reduced mechanism for carbon monoxide combustion, the fourth-order Rosenbrock method with four stages was chosen with a formula for adaptive control for the integration step. This method is L-stable, which is ideal for solving stiff systems, since they have maximally damped behavior. The code was implemented in the FORTRAN 90 language using double precision and a tolerance for error $\varepsilon = 10^{-7}$.

The mole fractions for carbon monoxide (left) and hydrogen (right) are shown in Figure 2. At the beginning of the process (up to time 10^{-4}) the main reaction is the I'. From the moment there is a higher concentration of H_2, reactions II' and III' stand out and water is produced again. At the moment the carbon monoxide is fully consumed, the CO_2 concentration stabilizes.
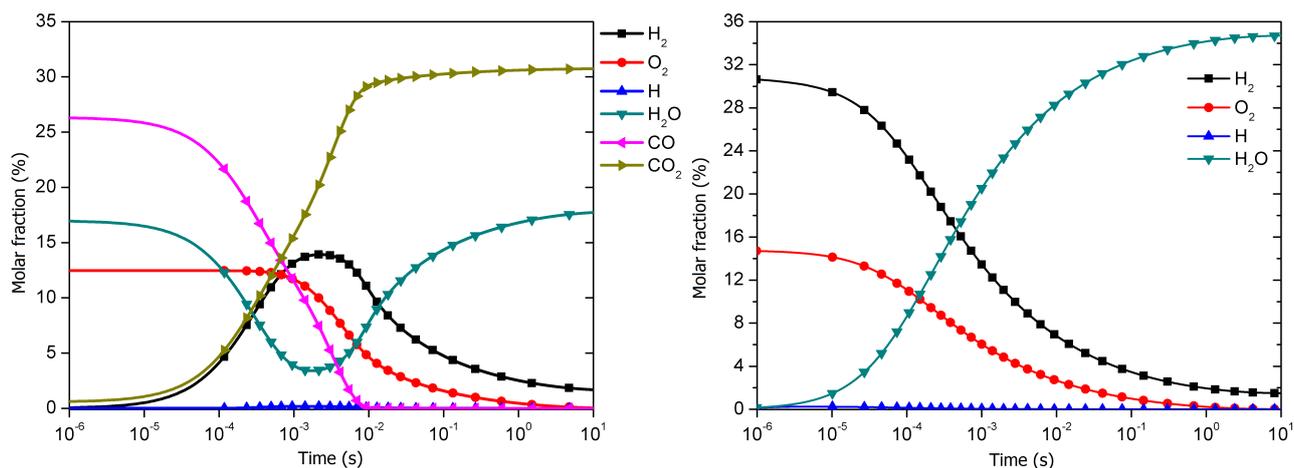

Figure 2. Mole fraction of CO (left) and H_2 (right) combustion in relation to time.

The data of H_2 can be compared to the results from Gaseq. Gaseq uses a method for calculating equilibrium compositions at a specified temperature based on the minimization of free energy (NASA method). The comparison of the mole fraction obtained in H_2 combustion with that provided by Gaseq is shown next.

While this work presents values of mole fraction in equilibrium of O_2, H_2, H_2O and N_2 as 0%, 1.492%, 34.7% and 63.8%, Gaseq brings them as 0.6%, 1.5%, 32,4% and 64.6%, respectively. The result was satisfactory considering that there was an average error of less than one percent.

4. CONCLUSION

In this work was desenvolved a strategy for reduce the combustion mechanism of carbon monoxide and hydrogen. The reduced mechanism for carbon monoxide present 3 steps and 6 chemical species, while the reduced mechanism for hydrogen present 2 steps and 4 chemical species. This is a strategy to minimize the stiffness of chemical kinetic mechanisms, contributing for a significant reduction in the computational cost, approximately one order of magnitude. For the carbon monoxide it had a total burn of CO during the process, having CO_2 and H_2O as a final product. For the hydrogen, the simulated mechanism, it had a total consumption of H_2, resulting just H_2O at the end of the simulation, as physically expected. This procedure justifies the Hydrogen as a potential clean source of energy. Using the initial and boundary conditions, this shows good data consistency when applies the Rosenbrock method and is in agreement with data found in the literature.

5. ACKNOWLEDGEMENTS

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