17th Brazilian Congress of Thermal Sciences and Engineering
November 25th-28th, 2018, Águas de Lindóia, SP, Brazil

ENCIT-2018-0291
ASYMPTOTIC ANALYSIS OF METHANE REDUCED KINETIC MECHANISM

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Abstract. *This work presents the chemical reactions required to model the combustion of methane, including the sub-mechanisms of carbon monoxide and hydrogen, which are important in the oxidation of other hydrocarbons and larger biofuels, such as methanol and ethanol. These models present a high degree of stiffness, which makes numerical resolution of the systems of ordinary differential equations difficult. In order to moderate the degree of stiffness and decrease the number of species involved, a four-step strategy is applied to obtain reduced mechanisms. A four-step mechanism for methane with seven chemical species is shown - including a three-step mechanism for carbon monoxide and a two-step for hydrogen - and the numerical results for the mass fraction is presented.*

Keywords: *methane, combustion, Rosenbrock, stiffness.*

1. INTRODUCTION

Methane is the main constituent of natural gas and biogas. Natural gas is a fossil fuel, a mixture of hydrocarbons that is in the gaseous state under normal atmospheric conditions and is the result of the fossil organic matter decomposition inside the Earth. A possible substitute for natural gas is biogas. Both fuels have the same formation process, through the anaerobic decomposition of the organic matter. The difference between them is that natural gas is not formed by the circulation of the organic material present on the earth's surface. On the other hand, when the organic material is converted to biogas, there is no additional release of carbon dioxide, but, taking advantage of the energy potential that is stored in organic matter.

Methane naturally forms at all times in environments with absence of oxygen, for example from marshes, soils, sediments of lakes, rivers and seas. According to Karlsson (2014) this raw biogas usually consists of a third of methane, a third of other gases (H_2S, O_2 and NH_3) and a third of CO_2. The biogas may then go to a purification process to generate the biomethane, which consists in dissolving the H_2S and CO_2 gases by washing with pressurized water or with other chemicals. In addition, the biodigestion treatment of the substrates eliminates pathogens, which allows the application of post-treatment residue in the soil for use as fertilizer.

Some mechanisms were obtained and published in the 1990s for premixed and nonpremixed flames (Peters (1992) and Peters and Rogg (2008)). For the methane oxidation it can be used several mechanisms, some with 15 chemical species and 35 elementary reactions (Peters, 1992), while others with more than 300 elementary reactions among more than 30 chemical species (Liu *et al.*, 2003). Detailed mechanisms present a high degree of stiffness, which makes numerical resolution of the systems of ordinary differential equations difficult. In order to moderate the degree of stiffness and decrease the number of species and reactions involved, a four-step strategy is applied to obtain reduced mechanisms.

In what follows, we show this strategy using the hypothesis of partial equilibrium and steady-state; we check the reduced mechanism employing an asymptotic analysis and compare some numerical results with data found in the literature.

2. OBTAINING REDUCED MECHANISMS

Reaction mechanisms for combustion are important tools in considering advances in fuel and biofuels efficiency. In a growing area of study, where computational models have codes that become more complex with each advancement, finding simplifications that facilitate analysis and reduce computational cost is essential.

The proposed strategy for the reduction of the mechanism is:

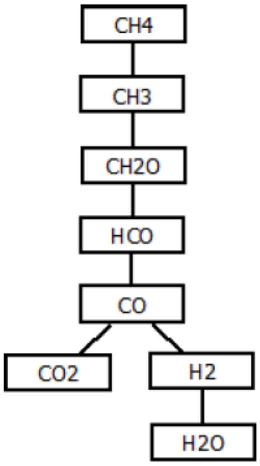

Figure 1. Preferential path for the combustion of methane.

1. Estimate the order of magnitude for the reaction rates.
2. Define the main chain.
3. Apply the steady-state and partial equilibrium hypothesis.
4. Justify the hypothesis by an asymptotic analysis.

In a homogeneous system, the steady-state hypothesis is valid for intermediate species that are produced by slow reactions and consumed by fast reactions, which means that their concentrations remain small (Turns, 2000). According to Peters (1988), the partial equilibrium hypothesis is justified when the velocities of forward and backward reactions are much larger than the other specific velocities of the mechanism.

The specific velocity k of each elementary reaction is given by the relation

$$k_\kappa = AT^\beta \exp\left(-\frac{E_A}{RT}\right), \tag{1}$$

where A is the frequency factor, T the temperature, β the temperature exponent, E_A the activation energy and R the gas constant. From these values, the magnitude of the reaction rates is estimated and the main chain of the combustion process is defined.

2.1 Reduced kinetic mechanism for methane

For methane flames with poor stoichiometry, a skeletal mechanism of 25 elementary reactions of Table 1 was identified as a sufficiently good representation of elementary kinetics by Peters (1992). The preferential path of reactions for the methane combustion is presented in the Figure 1, and is obtained from the analysis of the specific velocity of each elementary reaction, considering $T = 800K$.

After applying the hypothesis of partial equilibrium for those reactions with high specific forward and backward velocities, it remains the reactions 1f, 1b, 2f, 2b, 3f, 3b, 9f, 10f, 14, 16, 18, 20 e 25. Considering the steady-state assumption for the species CH_3, CH_3O, CH_2O, HCO, OH and O, it results the following four-step mechanism among seven species for methane

$$\begin{array}{l} I' \quad CH_4 + 2H + H_2O = CO + 4H_2 \\ II' \quad CO + H_2O = CO_2 + H_2 \\ III' \quad 3H_2 + O_2 = 2H + 2H_2O \\ IV' \quad H + H + M = H_2 + M \end{array} \tag{2}$$

The reduced mechanism obtained for methane can be justified by asymptotic analysis. For the set of elementary reactions presented in Table 1, the balance equations for methane can be written as

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

	Reaction	A	β	E_A
1f	$H + O_2 \rightarrow O + OH$	$2.000E + 14$	0.00	16800
1b	$O + OH \rightarrow O_2 + H$	$1.575E + 13$	0.00	690
2f	$O + H_2 \rightarrow OH + H$	$1.800E + 10$	1.00	8826
2b	$OH + H \rightarrow O + H_2$	$8.000E + 09$	1.00	6760
3f	$H_2 + OH \rightarrow H_2O + H$	$1.170E + 09$	1.30	3626
3b	$H_2O + H \rightarrow H_2 + OH$	$5.090E + 09$	1.30	18588
4f	$OH + OH \rightarrow H_2O + O$	$6.000E + 08$	1.30	0
4b	$H_2O + O \rightarrow OH + OH$	$5.900E + 09$	1.30	17029
5	$H + O_2 + M \rightarrow HO_2 + M$	$2.300E + 18$	-0.80	0
6	$H + HO_2 \rightarrow OH + OH$	$1.500E + 14$	0.00	1004
7	$H + HO_2 \rightarrow H_2 + O_2$	$2.500E + 13$	0.00	700
8	$OH + HO_2 \rightarrow H_2O + O_2$	$2.000E + 13$	0.00	1000
9f	$CO + OH \rightarrow CO_2 + H$	$1.510E + 07$	1.30	-758
9b	$CO_2 + H \rightarrow CO + OH$	$1.570E + 09$	1.30	22337
10f	$CH_4 + M \rightarrow CH_3 + H + M$	$6.300E + 14$	0.00	104000
10b	$CH_3 + H + M \rightarrow CH_4 + M$	$5.200E + 12$	0.00	-1310
11f	$CH_4 + H \rightarrow CH_3 + H_2$	$2.200E + 04$	3.00	8750
11b	$CH_3 + H_2 \rightarrow CH_4 + H_2$	$9.570E + 02$	3.00	8750
12f	$CH_4 + OH \rightarrow CH_3 + H_2O$	$1.600E + 06$	2.10	2460
12b	$CH_3 + H_2O \rightarrow CH_4 + OH$	$3.020E + 05$	2.10	17422
13	$CH_3 + O \rightarrow CH_2O + H$	$6.800E + 13$	0.00	0
14	$CH_2O + H \rightarrow HCO + H_2$	$2.500E + 13$	0.00	3991
15	$CH_2O + OH \rightarrow HCO + H_2O$	$3.000E + 13$	0.00	1195
16	$HCO + H \rightarrow CO + H_2$	$4.000E + 13$	0.00	0
17	$HCO + M \rightarrow CO + H + M$	$1.600E + 14$	0.00	14700
18	$CH_3 + O_2 \rightarrow CH_3O + O$	$7.000E + 12$	0.00	25652
19	$CH_3O + H \rightarrow CH_2O + H_2$	$2.000E + 13$	0.00	0
20	$CH_3O + M \rightarrow CH_2O + H + M$	$2.400E + 13$	0.00	28812
21	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.000E + 12$	0.00	0
22f	$H_2O_2 + M \rightarrow OH + OH + M$	$1.300E + 17$	0.00	45500
22b	$OH + OH + M \rightarrow H_2O_2 + M$	$9.860E + 14$	0.00	-5070
23f	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$1.000E + 13$	0.00	1800
23b	$H_2O + HO_2 \rightarrow H_2O_2 + OH$	$2.860E + 13$	0.00	32790
24	$OH + H + M \rightarrow H_2O + M$	$2.200E + 22$	-2.00	0
25	$H + H + M \rightarrow H_2 + M$	$1.800E + 18$	-1.00	0

$$
\begin{aligned}
L(C_{H_2}) &= -\omega_2 - \omega_3 + \omega_7 + \omega_{11} + \omega_{14} + \omega_{16} + \omega_{19} + \omega_{25}, \\
L(C_H) &= -\omega_1 + \omega_2 + \omega_3 - \omega_5 - \omega_6 - \omega_7 + \omega_9 + \omega_{10} - \omega_{11} \\
&\quad +\omega_{13} - \omega_{14} - \omega_{16} + \omega_{17} - \omega_{19} + \omega_{20} - \omega_{24} - 2\omega_{25}, \\
L(C_{O_2}) &= -\omega_1 - \omega_5 + \omega_7 + \omega_8 - \omega_{18} + \omega_{21}, \\
L(C_O) &= +\omega_1 - \omega_2 + \omega_4 - \omega_{13} + \omega_{18}, \\
L(C_{H_2O}) &= +\omega_3 + \omega_4 + \omega_8 + \omega_{12} + \omega_{15} + \omega_{23}\omega_{24}, \\
L(C_{OH}) &= +\omega_1 + \omega_2 - \omega_3 - 2\omega_4 + 2\omega_6 - \omega_8 - \omega_9 - \omega_{12}\omega_{15} + 2\omega_{22} - \omega_{23} - \omega_{24}, \\
L(C_{HO_2}) &= +\omega_5 - \omega_6 - \omega_7 - \omega_8 - 2\omega_{21} + \omega_{23}, \\
L(C_{H_2O_2}) &= +\omega_5 - \omega_6 - \omega_7 - \omega_8 - 2\omega_{21} + \omega_{23}, \\
L(C_{CO}) &= -\omega_9 + \omega_{16} + \omega_{17}, \\
L(C_{CO_2}) &= +\omega_9, \\
L(C_{CH_4}) &= -\omega_{10} - \omega_{11} - \omega_{12}, \\
L(C_{CH_3}) &= +\omega_{10} + \omega_{11} + \omega_{12} - \omega_{13} - \omega_{18}, \\
L(C_{CH_3O}) &= +\omega_{18} - \omega_{19} - \omega_{20}, \\
L(C_{CH_2O}) &= +\omega_{13} - \omega_{14} - \omega_{15} + \omega_{19} + \omega_{20}, \\
L(C_{HCO}) &= +\omega_{14} + \omega_{15} - \omega_{16} - \omega_{17}.
\end{aligned}
\tag{3}
$$

where $L(C_i)$ denotes a linear differential operator applied to the concentration of the species i and ω_κ represents the reaction rate of the reaction κ. The plus sign refers to species that appear on the right side of an elementary reaction, while the minus sign refers to species on the left.

Assuming the steady-state hypothesis for the species O, OH, HO_2, H_2O_2, CH_3, CH_3O, CH_2O and HCO, so $L(C_i)$ are zero in this equations, which leads to eight algebraic equations among the reaction rates ω_κ:

$$\begin{aligned}
&\omega_2 = +\omega_1 + \omega_4 - \omega_{10} - \omega_{11} - \omega_{12} + 2\omega_{18}, \omega_7 = -\omega_5 - \omega_6 - \omega_8 - 2\omega_{21} + \omega_{23},\\
&\omega_{13} = +\omega_{10} + \omega_{11} + \omega_{12} - \omega_{18}, \omega_{15} = +\omega_{10} + \omega_{11} + \omega_{12} - \omega_{14},\\
&\omega_{16} = +\omega_{10} + \omega_{11} + \omega_{12} - \omega_{17}, \omega_{19} = +\omega_{18} - \omega_{20}, \omega_{22} = +\omega_{21} - \omega_{23},\\
&\omega_{24} = - + 2\omega_1 - \omega_3 - \omega_4 + 2\omega_6 - \omega_8 - \omega_9 - 2\omega_{10} - 2\omega_{11} - 3\omega_{12} + \omega_{14} + 2\omega_{18} + 2\omega_{21} - 3\omega_{23}.
\end{aligned} \tag{4}$$

Making the rates $\omega_{I'}$, $\omega_{II'}$, $\omega_{III'}$ and $\omega_{IV'}$ equal to

$$\begin{aligned}
&\omega_{I'} = \omega_{10} + \omega_{11} + \omega_{12},\\
&\omega_{II'} = \omega_9,\\
&\omega_{III'} = \omega_1 + \omega_6 + \omega_{18} + \omega_{21} - \omega_{23},\\
&\omega_{IV'} = 2\omega_1 - \omega_3 - \omega_4 + \omega_5 + 2\omega_6 - \omega_8 - \omega_9 - 2\omega_{10} - \omega_{11} - 2\omega_{12} + \omega_{14} - \omega_{17} + 2\omega_{18} - \omega_{20} + \omega_{21} - 2\omega_{23} + \omega_{25},
\end{aligned} \tag{5}$$

one obtains the following linear combinations

$$\begin{aligned}
&L(C_{H_2}) = +4\omega_{I'} + \omega_{II'} - 3\omega_{III'} + \omega_{IV'},\\
&L(C_H) = -2\omega_{I'} + 2\omega_{III'} - 2\omega_{IV'},\\
&L(C_{O_2}) = -\omega_{III'},\\
&L(C_{H_2O}) = -\omega_{I'} - \omega_{II'} + 2\omega_{III'},\\
&L(C_{CO}) = +\omega_{I'} - \omega_{II'},\\
&L(C_{CO_2}) = +\omega_{II'},\\
&L(C_{CH_4}) = -\omega_{I'}.
\end{aligned} \tag{6}$$

The stoichiometry of these balance equations corresponds to the global mechanism (2) of four-step for the methane, which includes the three-step mechanism for the carbon monoxide (II', III' and IV') and the two-step for hydrogen (reactions III' and IV').

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 fourth-order four-stage Rosenbrock method is given by:

$$y_{n+1} = y_n + h\sum_{i=1}^{4} \gamma_i \kappa_i \tag{7}$$

$$\kappa_1 = f(y_n)/A(y_n) \tag{8a}$$

$$\kappa_2 = f(y_n + ha_{21}\kappa_1)/A(y_n) \tag{8b}$$

$$\kappa_3 = f(y_n + h(a_{31}\kappa_1 + a_{32}\kappa_2))/A(y_n) \tag{8c}$$

$$\kappa_4 = f(y_n + h(a_{41}\kappa_1 + a_{42}\kappa_2 + a_{43}\kappa_3))/A(y_n) \tag{8d}$$

where

$$A(y_n) = \left[I - hd\frac{\partial f(y_n)}{\partial y}\right]. \tag{9}$$

The local error estimate is

$$E_{n+1} = \frac{\|y^*_{n+1} - y_{n+1}\|}{(2^\rho - 1)} \tag{10}$$

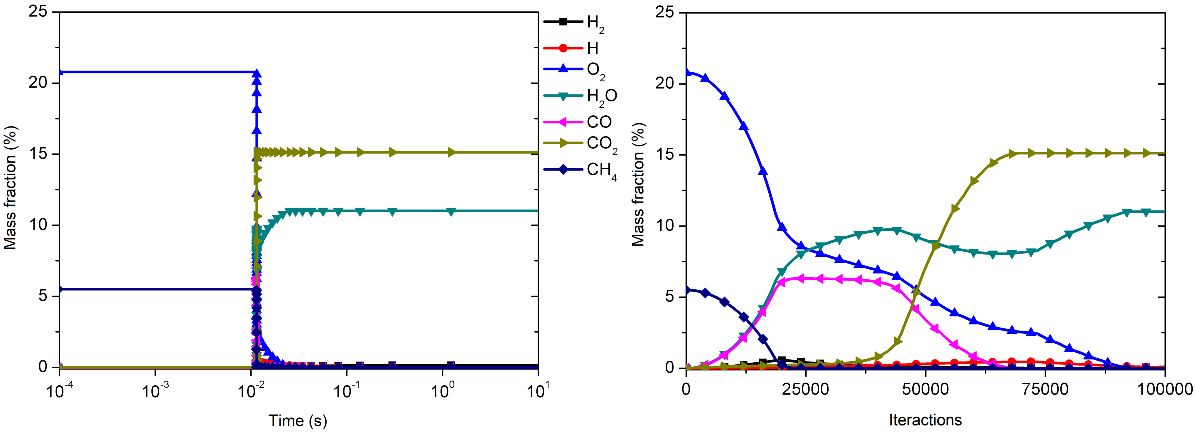

Figure 2. Mass fraction of CH_4 combustion in relation to time and interactions.

where ρ is the order of the method and the norm $\| \cdot \|$ is given by

$$\|y\| = \left[\frac{1}{\phi} \sum_{i=1}^{\phi} \left(\frac{y_{n+1}^i}{y_{max}^i} \right)^2 \right]^{1/2}, \tag{11}$$

where ϕ is the number of species involved in the mechanism.

The overall error estimate is:

$$Eg_{n+1} = max(|y(n+1) - y^{*,2}|), \tag{12}$$

where $y^{*,2}$ is obtained by Rosenbrock method using step size $h/2$ and $y^{*,1}$ as initial condition, being that $y^{*,1}$ was calculated with step size h and with y_n as initial condition.

Taking into account a tolerance ϵï£¡, one can choose the procedure below to determine the time increment:

- If $E_{n+1}\epsilon$, the increment is rejected and h should be reduced.
- If $3\epsilon/4 < E_{n+1} < \epsilon$ï£¡, the increment is accepted, but h should be reduced.
- If $\epsilon/10 < E_{n+1}\epsilon$ï£¡, the increment is accepted and h should be sustained.
- If $E_{n+1} < \epsilon/10$ the increment is accepted and h can be increased.

The code was implemented in the Fortran 90 language using double precision and a tolerance for error $\varepsilon = 10^{-8}$. For the resolution of the linear system of each stage in each iteration the successive sub-relaxation method (SUR) was used. The numerical results of the process are shown in Figure 2. The methane combustion graphs are presented in relation to time and in relation to the number of iterations, since the process occurs in an interval of integration very small and difficult to visualize in graphs, even on a logarithmic scale.

The data of CH_4 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 mass fraction obtained in CH_4 combustion with that provided by Gaseq is shown in Table 2.

Table 2. Comparison of the mass fraction obtained in CH_4 combustion with Gaseq.

Species	This work	Gaseq
H_2O	11,013%	12%
CO_2	15,132%	14%
O_2	0%	0,5%
N_2	72,6%	72,4%

The result was satisfactory considering that there was an average error of less than one percent. In a growing area of study, where computational models have codes that become more complex with each advancement, finding simplifications that facilitate analysis and reduce computational expenditure is essential. In this way, the simplifications used in this work contribute to the achievement of good results, with reduced stiffness of the system.

The main advantage of the reduction of the mechanism is the decrease of the work required to solve the system of equations. The time required for the resolution of chemical equations reduces by an order of magnitude for methane, since the number of equations decreases in that order. For the continuity of this work, it is intended to simulate reduced mechanisms of larger molecules of biofuels, such as methanol and ethanol, for example.

4. ACKNOWLEDGEMENTS

This research is being developed at UFPel, Federal University of Pelotas, and at UFRGS, Federal University of Rio Grande do Sul. R. Sehnem thanks the financial support from Brazilian federal government agency CAPES.

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