NUMERICAL SIMULATIONS OF KINETIC COMBUSTION MECHANISMS OF METHANOL AND ETHANOL BY ROSENBROCK METHOD

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ABSTRACT

In this article, we present the use of an implicit method for simulating reduced combustion mechanisms of methanol and ethanol. The Rosenbrock method was used to obtain the result with greater stability in the simulation of the ODE system obtained through the reduced mechanisms. In the numerical results, some simulations are presented for the reduced mechanisms of methanol and ethanol. The commercial software Gaseq is used to analyze the results obtained in this work, presenting good agreement and showing that the Rosenbrock method is effective for resolving the extreme rigid EDO system regarding the chemical kinetics of these mechanisms.

INTRODUCTION

Energy sources have become determinant factors in the quality of life in all stages of human history, considering that they promote social and economic development, establishing the structure of each society (Rizzo; Pires, 2005). Coal, oil and gas in addition to nuclear energy, hydropower and biofuels are traditional energy sources. Among them, there is a predominance of fossil fuels that basically comprise natural gas, oil and coal, which are the result of the decomposition of organic matter deposited millions of years ago in the soil (Alves et al., 2012).Although huge, fossil fuel reserves are limited. To reduce the demand on these fuels, biofuels are being studied as they are renewable and reduce the emission of gases that cause the greenhouse effect (Atkins; Paula, 2012). The main biofuels currently used are ethanol, methanol, biogas and biodiesel. Methanol and ethanol are chemical compounds of formulas CH_3OH and C_2H_5OH, respectively.The complete methanol mechanism contains 129 reactions and 31 species (Andreis,2011) and the ethanol oxidation mechanism consists

of 372 reactions and 56 species (Vaz,2013). The models produced by chemical kinetics of reactions, when made with detailed mechanisms, are difficult to solve, first due to the largenumber of reactions and species and secondly due to the existence of highly reactive radicals, which leads to the stiffness of the system of equations. Therefore, reduced kinetic mechanisms are preferred, as they reduce the stiffness of the system, the dimension and, consequently, the computational time of processing and storing the data necessary for a numerical simulation (Andreis,2011).The kinetic mechanisms generate systems of stiff ordinary differential equations (ODE's) subject to the initial conditions and their solutions require numerical methods, so that the solutions are stable at an acceptable computational cost. Although problems with stiff ODE systems are frequent, there is no known mathematically precise definition to describe this characteristic. Stiff problems require implicit methods to have the required stability region (Curtiss; Hirschfelder, 1952).Shampinee Gear (1979 obtained many experiences in computational tests, providing a definition: an initial value

problem for an ODE system is only stiff if the Jacobian matrix of the system has at least one eigenvalue for which the real part is negative and with a large module, while the solution over most of the integration interval changes slowly. This is the definition that best characterizes stiffness, showing that these problems present solutions in which some components decrease much more quickly than others.This work aims to apply an implicit method, so that results are obtained with greater stability in the simulation of ODE systems generated by the reduced combustion mechanisms of methanol and ethanol.

METHODOLOGY

In this section we will discuss fundamental definitions for the development of this work, such as the reduction of mechanisms and the numerical method used. SectionII.A is based on the work of Vaz (2013) and the books of Peters (1992) and Turns (2013).Section II.B is based on the book by Kuo (2005).

Variables of interest: Combustion is the conversion of a fuel into energy, in the form of heat and light. In a combustion process, the chemical bonds in the molecules of a fuel and an oxidizer are broken. The atoms present are reorganized, in the form of products of combustion, new connections are made. As a result, in addition to combustion products, thermal energy is released.To quantitatively describe the chemical transformation between species, we need to introduce fundamental concepts and definitions.

Molar Fraction: The molar fraction is a way of representing the concentration of the countless chemical species present in the mixture. For each component$i$, the molar fraction X_i is the numberof moles n_i divided by the number of moles of the n_{ts} system, that is:

$$X_i = \frac{n_i}{n_{ts}}, \tag{1}$$

The number of moles in the system being given by:

$$n_{ts} = \sum_{i=1}^{n_{sp}} n_i, \tag{2}$$

wheren_{sp} is the total number of species in the system.

Mass Fraction

The mass m_i of all molecules of the species i is related to the number of moles by:

$$m_i = W_i n_i, \tag{3}$$

where W_i is the molar mass of specie i.

The total mass for all species in the mixture is:

$$m_{ts} = \sum_{i=1}^{n_{sp}} m_i. \tag{4}$$

The mass fraction of species i is represented by the ratio of its mass to the total massof the system by:

$$Y_i = \frac{m_i}{m_{ts}}. \tag{5}$$

Therefore, the relationship between the mass fraction and the molar fraction is obtained:

$$Y_i = \frac{W_i}{W} X_i, \tag{6}$$

where W is the average molar mass in number, given by:

$$W = \left[\sum_{i=1}^{n_{ts}} \frac{Y_i}{W_i} \right]^{-1}. \tag{7}$$

Molar concentration: An intensive property of the system that defines the number of moles per unit volumeis the molar concentration, given by the equation:

$$[X_i] = \frac{n_i}{V}, \tag{8}$$

where V is the volume of the system.

The relationship between concentration and mass and molar fraction is:

$$[X_i] = \frac{\rho_i}{W_i} Y_i = \frac{\rho_i}{W} X_i, \tag{9}$$

where$\rho_i$is the specific mass of species i.

B. Chemical Kinetics

Chemical kinetics is the part of chemical science that is dedicated to the quantitative study of chemical reaction rates and factors on which they depend.A one-step chemical reaction, of arbitrary complexity, can be represented by the following stoichiometric equation:

$$\sum_{i=1}^{N} \nu_i' M_i \rightarrow \sum_{i=1}^{N} \nu_i'' M_i, \tag{10}$$

where coefficients ν_i' are the stoichiometric of the reagents, ν_i'' are the stoichiometric of the products, M_i the specification of the molecule of the chemical species, and N the total number of compoundsinvolved.

According to Kuo (2005), the law of mass action states that the reaction rate of a species of chemical product is proportional to the products of the concentrations of the reactive chemical species, with each concentration raised to a power equal to the corresponding stoichiometric coefficient. Thus, the reaction rate is given as:

$$\omega = \frac{d[product]}{dt} = \frac{d[reagent]}{dt} = k \prod_{i=1}^{N} [M_i]^{\nu_i'}, \tag{11}$$

where the k coefficient is the proportionality constant called the specific reaction rate. For a given chemical reaction, k is independent of the concentrations $[M_i]$ and depends only on the temperature. In general, k is expressed as:

$$k = AT^\beta \exp\left(-\frac{E_a}{R_u T}\right) \qquad (12)$$

where A is a frequency term (pre-exponential coefficient), T the temperature, β the temperature exponent, E_a the activation energy and R_u the universal constant of the ideal gases. The values of A, β and E_a are based on the nature of the elementary reaction.

The observable results of a chemical reaction are the net rates of change for the chemical components. From equations (10) and (11), we obtain the net production rate of M_i is:

$$\frac{d[M_i]}{dt} = (\nu_i'' - \nu_i')\omega = (\nu_i'' - \nu_i')k_f \prod_{i=1}^{N}[M_i]^{\nu_i'}. \qquad (13)$$

As M_i species can appear on both sides of the equation (10), with different values for ν_i'' and ν_i', the difference $(\nu_i'' - \nu_i')$ is multiplied by the reaction rate in the above equation. You can write expressions for each of the species involved in the mechanism, obtaining a system of first order differential equations. This ODE system has coefficients with significant differences in magnitude and also sudden changes in the behavior of its variables, which characterizes a stiffness for this type of problem. For this reason, reduced kinetic mechanisms are preferred, as they moderate the stiffness of the system.

C. Reduced Mechanism

Combustion mechanisms for fuels and biofuels are described by extremely stiff ODE systems. These models obtained by chemical kinetics have a high degree of stiffness, due to the existence of highly reactive radicals. Therefore, it is necessary to develop reduced mechanisms with fewer variables and with moderate stiffness, maintaining good precision and the general behavior of the mechanism(Lu; Law, 2006).In this work, we will use the systematic reduction method, which applies the hypotheses of steady state for intermediate species and partial equilibrium for fast reactions. The steady state is based on the hypothesis that these intermediate species of the complete mechanism do not contribute significantly to the determination of the rate that governs the combustion process in general. Partial equilibrium is related to reactions that have a direct and inverse reaction rate in equilibrium(Vaz, 2013).The reduced kinetic mechanisms have the main benefit of reducing the computational effort for the numerical simulation of the system involved, replacing the differential equations for intermediate species, which are assumed to exist in the permanent regime, by algebraic relations(DeBortoli; Andreis, 2010).Hereafter, the reduced kinetic mechanisms are presented using the hypotheses of steady state and partial equilibrium.

Methanol

The methanol combustion is an example of a stiff kinetic mechanism. The complete mechanism of methanol is presented by Marinov(1999)containing 129 reactions and 31 species, a preferential path for the combustion of methanol is shown in Figure 1, in which there are monoxide carbon (CO) and hydrogen (H_2). This path is determined through an analysis of the specific velocity of each elementary reaction, from equation (12), with a temperature of 800 K and the factors A, E and β defined byMarinov (1999).
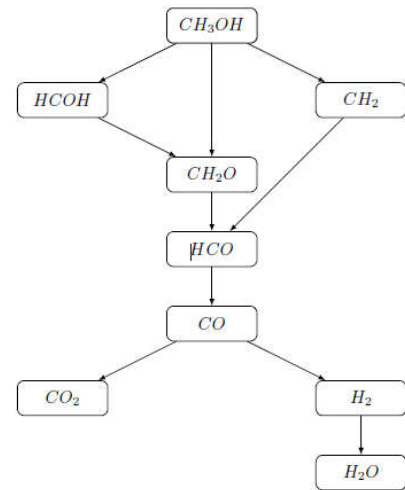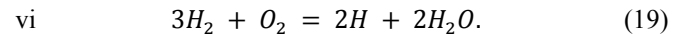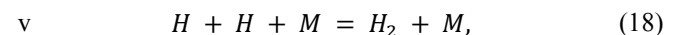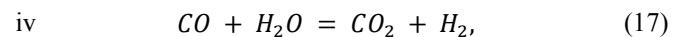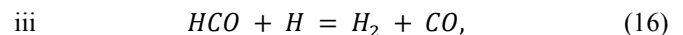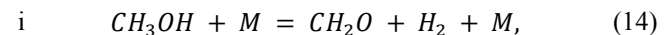

Figure 1. Main chain diagram of the reduced methanol mechanism

From this preferential path, a reduction strategy is used, based on concepts of chemical kinetics, developed byAndreis (2011), a reduced mechanism for methanol with 6 reactions and 9 species is reached, which is expressed as:

i $\qquad CH_3OH + M = CH_2O + H_2 + M,$ $\qquad (14)$

ii $\qquad CH_2O + M = HCO + H + M,$ $\qquad (15)$

iii $\qquad HCO + H = H_2 + CO,$ $\qquad (16)$

iv $\qquad CO + H_2O = CO_2 + H_2,$ $\qquad (17)$

v $\qquad H + H + M = H_2 + M,$ $\qquad (18)$

vi $\qquad 3H_2 + O_2 = 2H + 2H_2O.$ $\qquad (19)$

Ethanol: Thecomplete ethanol oxidation mechanism presented by Marinov (1999), is formed by 56 species and 372 reversible reactions. Analyzing the order of magnitude of elementary reactions, by calculating the specific velocities (k), using the equation (12). The preferred path for ethanol combustion is obtained, with T=900 K and R=1.98 cal/(mol/K), shown in Figure 2. The values of A, β and E are provided byMarinov (1999). This analysis is validated for temperatures above 600 K.
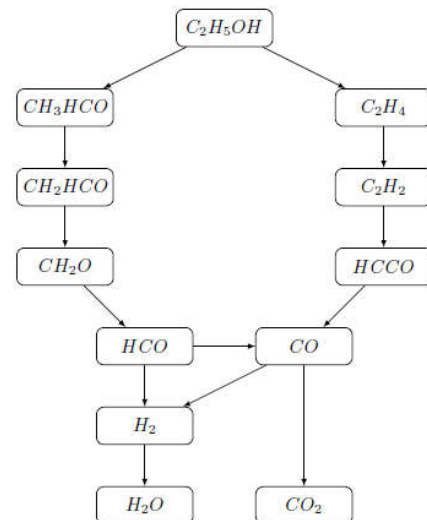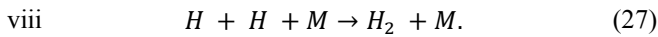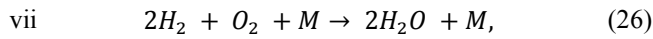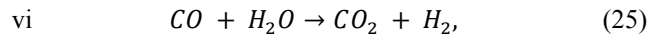

Figure 2 Main chain diagram of the reduced ethanol mechanism

From this preferential path, a reduction method is used, based on the work of Vaz (2013). Therefore, the full mechanism

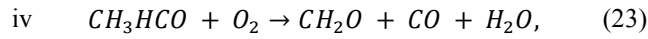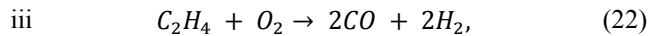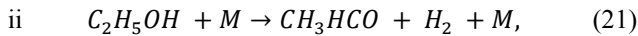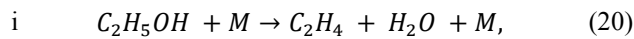consisting of 372 reactions and 56 species is simplified to a reduced mechanism with 8 reactions and 10 species.

i $C_2H_5OH + M \rightarrow C_2H_4 + H_2O + M,$ (20)

ii $C_2H_5OH + M \rightarrow CH_3HCO + H_2 + M,$ (21)

iii $C_2H_4 + O_2 \rightarrow 2CO + 2H_2,$ (22)

iv $CH_3HCO + O_2 \rightarrow CH_2O + CO + H_2O,$ (23)

v $CH_2O + M \rightarrow CO + 2H + M,$ (24)

vi $CO + H_2O \rightarrow CO_2 + H_2,$ (25)

vii $2H_2 + O_2 + M \rightarrow 2H_2O + M,$ (26)

viii $H + H + M \rightarrow H_2 + M.$ (27)
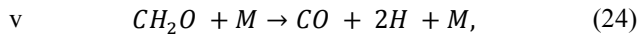
D. Rosenbrock method

Based on the linearization of the Runge-Kutta methods, Rosenbrock (1963) proposes a new class of L-stable methods. Its numerical advantage is the switch from solving non-linear systems to solving a sequence of linear systems(Sehnem, 2018). They depend.

A σ-stages Rosenbrock method is given by:

$$\kappa_i = hf\left(y_n + \sum_{j=1}^{i-1}\alpha_{ij}\kappa_j\right) + hJ\sum_{j=1}^{i}\gamma_{ij}\kappa_j,$$
$$i = 1,\dots,\sigma \qquad 28)$$
$$y_{n+1} = y_n + \sum_{i=1}^{\sigma} b_i\kappa_i,$$

where $J = J_f(y_n)$and the coefficients α_{ij}, γ_{ij} and b_i are determined in order to obtain an order of stability and consistency for stiff problems. Thus, Rosenbrock proposed the replacement of the Jacobian matrix calculated in g_i $(J_f(g_i))$ by $J_f(y_n) = J$, which brings computational gains since these factors are calculated only once. Multiplications $J \cdot k_j$ in the equations of κ_i are replaced by a multiplication with a linear combination of κ_j.The method used in this work is fourth order Rosenbrock with four stages, which is given by:

$$y_{n+1} = y_n + h\sum_{i=1}^{4}\gamma_i\kappa_i,\qquad(29)$$

$$\kappa_1 = \frac{f(y_n)}{A(y_n)},\qquad(30)$$

$$\kappa_2 = \frac{f(y_n + ha_{21}\kappa_1)}{A(y_n)},\qquad(31)$$

$$\kappa_3 = \frac{f(y_n + h(a_{31}\kappa_1 + a_{32}\kappa_2))}{A(y_n)},\qquad(32)$$

$$\kappa_4 = \frac{f(y_n + h(a_{41}\kappa_1 + a_{42}\kappa_2 + a_{43}\kappa_3))}{A(y_n)},\qquad(33)$$

According to Sartori (2014), Rosenbrock's methods are attractive due to automation in the control of the step size, always in accordance with the tolerance for local error.

NUMERICAL RESULTS

This section presents the numerical results obtained for methanol and ethanol. The Rosenbrock method was implemented for the two fuels in FORTRAN 90 language using double precision and imposing a tolerance of 10^{-7}, the integration interval was $[10^{-3}, 10^1]$.The results were compared with the Gaseq software that uses a numerical method based on the minimization of Gibbs free energy, that can be used as a tool to obtain the concentrations of the reagents and products of the chemical reactions of combustion (Morley, 2005). The main function of this software is to generate indicative data on emissions for different fuels - on this work, the combustion of methanol and ethanol.Air is considered to be a mixture composed of 23.7% of O_2 and 76.3% of N_2. The nitrogen (N_2) is inert in the combustion process and does not alter the chemical balance.

A. Methanol: The initial conditions of the oxidant $\left(\frac{3}{2}O_2\right)$ are used in relation to the fuel methanol (CH_3OH), requiring just over 0.6s to reach the chemical balance (remaining $2H_2O$ in relation to CO_2). Thus, Figure 3 shows a physically satisfactory result when compared to the methanol main chain with the global reaction, presented by Andreis (2011), for complete methanol combustion: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$.
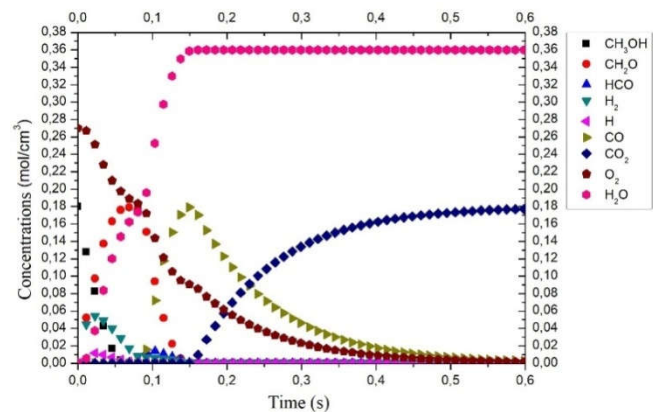
Figure 3 Simulation of concentrations of the reduced methanol mechanism

The initial molar fractions are: 13.43%of CH_3OH, 20.13% of O_2 and 66.44% of N_2. After the necessary conversions, the initial mass fractions are: 13.43% of CH_3OH, 20.12% of O_2 and 66.45% of N_2.
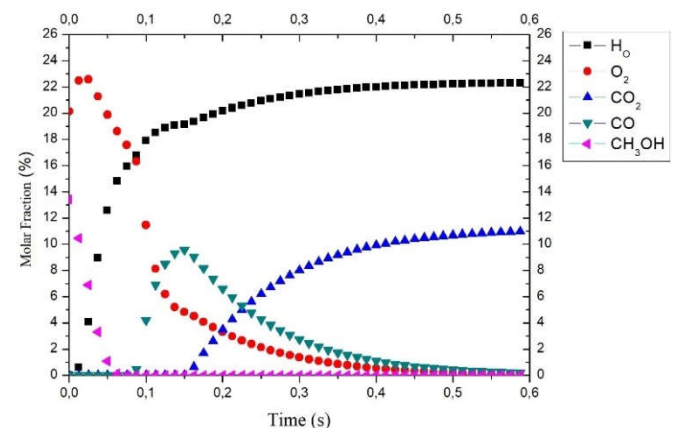
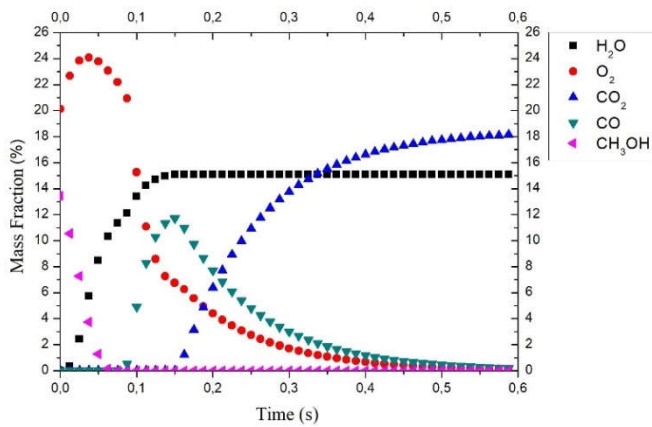**Figure 4. Molar fraction of methanol combustion**

Figure 5. Mass fraction of methanol combustion

Results of molar fractions and mass fractions of the products of methanol combustion were obtained using the Gaseq software. The comparisons of the data obtained through the Rosenbrock method (presented in Figures 4 and 5) with the data from the software are shown in Tables 1 and 2.

Table 1. Comparison of the molar fraction of the results obtained with the Gaseq software

Specie	Present work (%)	Gaseq (%)
H_2O	22.30	22.36
O_2	0.08	0.50
CO_2	11.00	10.50
CO	0.17	1.00
N_2	66.45	64.65

Table 2. Comparison of the mass fraction of the results obtained with the Gaseq software

Specie	Present work (%)	Gaseq (%)
H_2O	15.10	14.74
O_2	0.10	0.10
CO_2	18.17	16.87
CO	0.18	1.00
N_2	66.45	66.30

The results obtained through the Rosenbrock method are satisfactory compared to the Gaseq software, as it presents very similar results. It is also noteworthy that with the Rosenbrock method, it is possible to observe what happens to the concentrations of reagents and products during the combustion process.

B. Ethanol

To achieve chemical equilibrium for ethanol, approximately 0.30s was needed. The concentrations over the time interval can be seen in Figure 6. At a fixed temperature of 900K, the initial concentrations are composed of the reagents C_2H_5OH and O_2, where oxidizer ($3O_2$) is used in relation to the fuel (C_2H_5OH). As final products of ethanol combustion, there are considerable percentages of H_2O and CO_2, a satisfactory result when compared to the global reaction of ethanol $C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$ and its main chain shown in Figure 2.The initial molar fractions for ethanol are: 7.25% from C_2H_5OH, 21.74% from O_2 and 71.01% for N_2. The initial mass fractions for ethanol are: 10.12% from C_2H_5OH, 20.46 from O_2 and 69.42% for N_2. The numerical results obtained are shown in Figures 7 and 8 and comparisons with the literature are shown in Tables 3 and 4.
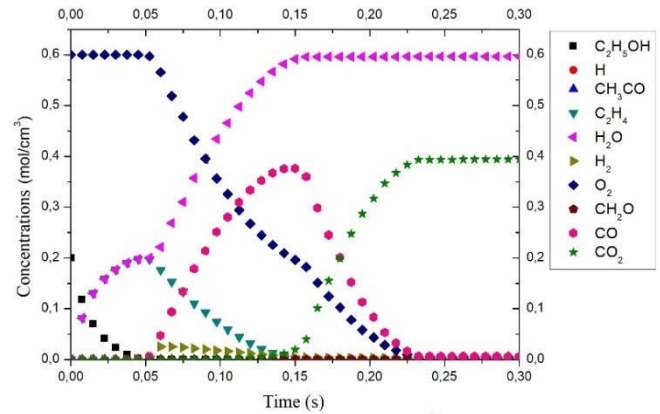

Figure 6. Simulation of the concentrations of the reduced ethanol mechanism
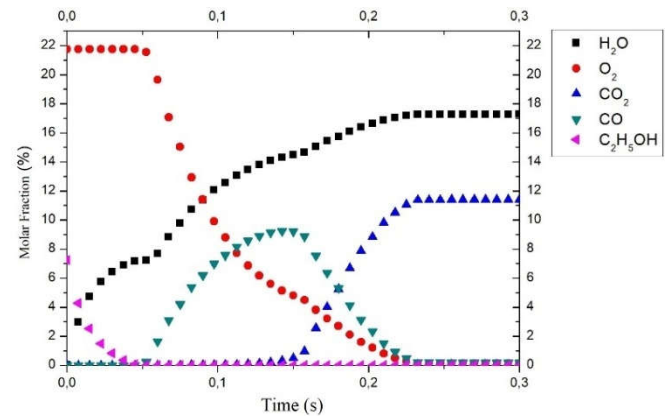

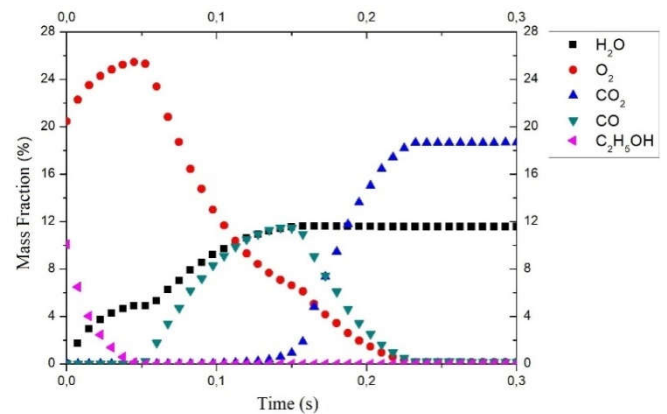**Figure 7. Molar fraction of ethanol combustion**

Figure 8. Mass fraction of ethanol combustion

Table 3. Comparison of the molar fraction of the results obtained with the Gaseq software, for the ethanol (C_2H_5OH)

Specie	Present work (%)	Gaseq (%)
H_2O	17.27	17.74
O_2	0.14	0.50
CO_2	11.42	10.70
CO	0.15	1.50
N_2	71.02	69.21

Table 4. Comparison of the mass fraction of the results obtained with the Gaseq software, for the ethanol (C_2H_5OH)

Specie	Present work (%)	Gaseq (%)
H_2O	11.56	11.50
O_2	0.16	0.60
CO_2	18.69	16.95
CO	0.16	1.60
N_2	69.43	68.72

Note that the results obtained show good agreement. It should be noted that through the results obtained for the concentration of ethanol (Figure 6), it is possible to visualize the behavior of each species throughout the combustion process.

Conclusion

This work seeks to collaborate in the environmental area through the study of reduced kinetic mechanisms of methanol and ethanol, serving to support research related to the application of biofuels as an energy source.The reduction and simplification of large kinetic mechanisms, such as biofuel mechanisms, brings several benefits to the study of the combustion process of biofuels, above all an efficient solution to the stiffness that large chemical systems present, thus enabling their numerical simulation and presenting significant reduction in computational costs.Through reduced kinetic mechanisms such as methanol and ethanol, it is possible to work with other higher-chain fuels. From these mechanisms, it was possible to understand the equations that represent the concentrations of chemical species involved in kinetic mechanisms, as well as to solve them numerically.The fourth order Rosenbrock method with four stages was chosen for the simulation and presented numerical stability necessary to obtain the results.The results presented show that the Rosenbrock method is effective for solving an extremely stiff ODE system from chemical kinetics, combustion of methanol and ethanol. The numerical results obtained through the Rosenbrock method for the combustion of methanol and ethanol presented satisfactory results when comparing the molar and mass fractions obtained with the Gaseq software.

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