DEVELOPMENT OF REDUCED REACTION MECHANISMS FOR C_1-C_6 HYDROCARBONS

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Abstract. Combustion is the result of exothermic chemical reactions between a fuel and an oxidizer. The release of heat can result in production of light in the form of a bright or a flame. The combustion of hydrocarbons is usually represented by a large number of chemical reactions, which constitute the full kinetic mechanism. Its use in computer models to simulate combustion processes may generate information to improve fuel quality and performance of the combustion process, and to quantify the emissions from this process. However, the use of full kinetic mechanisms generally complicates the numerical analysis of the process because of the excessive computational effort required. Due to this, it becomes important to develop reduced kinetic mechanisms for combustion processes, to reduce the computational effort in the numerical analysis of flames. Reduced mechanisms are obtained replacing the differential equations for the intermediate species, which are assumed to be in steady-state, by algebraic relations. This article aims to develop reduced kinetic mechanisms for C_1-C_6 hydrocarbons. Numerical values are compared with experimental data for the CO_2 and the results are in agreement.

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1 INTRODUCTION

Combustion processes are usually described through detailed kinetic mechanisms, i. e., at the level of elementary chemical steps. These mechanisms have several applications, including quantification of emissions from the combustion process and prediction of the amount of air required and fuel consumption. Generally, the greater the number of elementary steps of the mechanism, the greater its number of potential applications. However, the computational cost of simulations also increases with the number of elementary steps in the mechanism and, consequently, simplifications are often required for practical applications.

Various methods of reduction of kinetic mechanisms have been studied, including the computer singular perturbation (CSP) method by Lam (1993), the “lumping” method by Leung and Lindstedt (1995), the intrinsic low-dimensional manifolds (ILDM) by Ishmurzin et al. (2003) and sensitivity analysis by Muharam (2005). These methods are considered quantitative, implying the possible elimination of any important species or steps in the process.

The method proposed in this paper helps to deep the knowledge of how the global steps are obtained using quantitative and qualitative hypothesis. Such reduces the possibility of eliminating any reaction or species wrongly. Furthermore it:

i) Allows viewing the preferred route of the scheme;
ii) Considers the importance of each species in the mechanism;
iii) Is not influenced by other factors (pressure, temperature ,...).

Generally, the methods of reduction of kinetic mechanisms are based on the identification of species which are in steady-state. Species considered in steady-state are quickly consumed as soon as they are produced, not interfering in the combustion process, because their concentration remains small, with little variation during the reaction. Thus, the elementary reactions that involve species in steady-state are ignored, unless they are an important step in the mechanism.

Steady-state approximations for intermediate species can be justified in many different ways. For a homogeneous system, the steady-state hypothesis is valid for those intermediate species that are produced by slow reactions and consumed by fast reactions, such that their concentration remains small (Peters, 1992). They were first derived for zero dimensional homogeneous systems that depend only on time, and the term “steady-state" was introduced because the time derivative of the concentration of these species is set to zero, i. e.

$$\frac{d[\mathrm{C_i}]}{dt} = 0 = \sum_{k=1}^{r} \nu_{ik} w_k \tag{2}$$

where, t denotes the time, $\mathrm{C_i}$ concentration of specie i, ν_{ik} stoichiometric coefficient of specie i in the reaction k and w_k reaction rate.

According to Peters (1992), the steady-state assumption for a species i leads to algebraic equations for reaction rates. In this way, each of these equations eliminates rates in the remaining balance equations for the non-steady-state species. The stoichiometry of the resulting balance equations defines the global mechanism for the non-steady-state species. Therefore, the global mechanism depends on the choice of the reaction rates that are eliminated. The rule is that one should choose for each species the fastest rate by which it is consumed. Although this choice may be arbitrary sometimes, it has no consequence as far as the balance equations for the non-steady-state species are concerned.

The method presented in this article eliminates reactions involving species in steady-state. As an example, we can look at the attack of methane by the H radical, forming CH_3, which is soon consumed, producing CH_2O.

$$CH_4+H \rightarrow CH_3+H_2 \tag{A}$$

$$CH_3+O \rightarrow CH_2O+H \tag{B}$$

Now we assume that CH_3 radical is in steady-state because reaction B is faster than reaction A. One then can add both reactions, and cancel CH_3 to obtain the global reaction

$$CH_4+O \rightarrow CH_2O+H_2$$

in which the H also cancels, but this is fortuitous.

This method was used in a previous work for the combustion of simpler species: hydrogen, carbon monoxide, methane and ethylene (Martins et al., 2010) with satisfactory results.

This article aims to achieve a reduction in kinetic mechanisms for combustion of hydrocarbons, C_1-C_6, without compromising the accuracy of the model.

2 METHOLOGY

The identification of intermediate species at steady-state is made by comparing the magnitude of the specific rate (Eq. 1) of production and consumption of such species

$$k = BT^n \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where B is the frequency factor, n the exponent of the temperature, E the activation energy of the reaction considered and R the gas constant. Considering the range of combustion temperatures used for C_1-C_6 hydrocarbons, the temperature of 900 K was adopted as a reference, although the specific rate (k) is strongly temperature dependent.

The complete mechanism used as a basis to obtain reduced mechanisms for C_1-C_3 hydrocarbons was made by Peters (1992). For hydrocarbons of C_4 chain the complete mechanism was obtained from Frolov (2006). To obtain the reduced mechanism of pentane it was employed the full C_5-mechanism shown by Basevich (2009). Finally, we used the complete mechanism for C_6 hydrocarbons presented by Westbrook (2008).

3 RESULTS AND DISCUSSIONS

In this section the reduced mechanisms obtained are presented together with the results of the numerical analysis used to test them.

3.1 Reduced Mechanism

The reduced mechanisms obtained using steady-state hypothesis for some species are shown below. The results are presented separately for each of the hydrocarbons in the C_1-C_6 series.

3.1.1 Methane

The main consideration made while reducing the mechanism for methane combustion was to disregard the reactions of CH_4 with HO_2 for flame propagation, due to the small concentration of HO_2 and the large activation energy for the thermal decomposition of methane.

To obtain a 4-steps mechanism, steady-state can be assumed for CH_3, CH_2O, OH, O, resulting:

$$(\mathrm{I}_4)\ CH_4 + H_2O + 2H \leftrightarrow CO + 4H_2$$
$$(\mathrm{II}_4)\ CO + H_2O \leftrightarrow +CO_2 + H_2$$
$$(\mathrm{III}_4)\ H + H + M \leftrightarrow H_2 + M$$
$$(\mathrm{IV}_4)\ O_2 + 3H_2 \leftrightarrow 2H + 2H_2O$$

where M corresponds to a radical.

The step (I_4) shows the consumption of CH_4 for the formation of two major intermediates of the mechanism, CO and H_2. The choice of retaining H rather than OH or O as a non-steady-state species is justified because H appears as a reactant in the first reaction $H+O_2 \rightarrow O+OH$, which is the most important one for flame calculations. It competes with $H+O_2+M \rightarrow HO_2+\mathrm{M}$ as the most important chain breaking reaction. Therefore it is crucial to calculate the H concentration more accurately than those of O and OH (Peters, 1992).

3.1.2 Acetylene

The subset of chemical equations used as starting mechanism here constitutes the full C_1 - C_2 mechanism with the addition of C_3H_3 formation and consumption. Reactions of acetylene with O, OH and HO_2 are disregarded in this mechanism due to low concentrations of these radicals. It is obtained a 4-step mechanism assuming C_2H, $CHCO$ to be in steady-state.

$$(\mathrm{I}_4)\ C_2H_2 + O_2 \rightarrow 2CO + H_2$$
$$(\mathrm{II}_4)\ CO + H_2O \leftrightarrow CO_2 + H_2$$
$$(\mathrm{III}_4)\ H + H + M \rightarrow H_2 + M$$
$$(\mathrm{IV}_4)\ O_2 + 3H_2 \leftrightarrow 2H_2O + 2H$$

Contrary to methane, the formation of CO occurs by oxidation of the fuel. This is due to the fact that reactions of fuel and oxygen are more important than those of fuel and water in the case of acetylene.

3.1.3 Ethylene

The basic idea to obtain reduced mechanisms for ethylene flames is that the reaction of ethylene with *H* is an important reaction, leading to acetylene. The reactions with *O* are of less importance because of the lower concentration of O atoms. The thermal decomposition of ethylene and the reaction with CH_3 are unimportant for flame propagation.

The species C_2H_3, *CHCO*, CH_2, *CH* and *CHO* are considered to be in steady-state, due to the high values of their specific rates (about 10^{11}), leading to the following 5 global steps mechanism:

(I$_5$) $C_2H_4 + M \rightarrow C_2H_2 + H_2 + M$

(II$_5$) $C_2H_2 + O_2 \rightarrow 2CO + H_2$

(III$_5$) $CO + H_2O \leftrightarrow CO_2 + H_2$

(IV$_5$) $2H + M \rightarrow H_2 + M$

(V$_5$) $O_2 + 3H_2 \leftrightarrow 2H_2O + 2H$

It is clear that ethylene converts to acetylene and, as pointed before, this fuel oxidizes to form *CO*. This confirms that the developed method represents the combustion process adequately.

3.1.4 Propane

The main path for the combustion of propane ignores the reactions of propane with *O* and *OH,* and also with the reactions of C_2H_2, *OH* and *CH*. Besides, reactions of C_3H_7, C_3H_5 and C_3H_4, leading to the C_2-chains, are of minor importance. Assuming the steady-state hypothesis for the species C_3H_7, C_3H_5, C_3H_4, *CHO*, C_2H, *CHCO*, CH_2, *O*, and *OH*, it is obtained a 6-step mechanism for propane. Specific rates indicate that no steady-state is achieved for the species C_3H_6 and C_2H_4 for the mechanism of 6 steps. Thus, it is obtained:

(I$_6$) $C_3H_8 \rightarrow C_3H_6 + H_2$

(II$_6$) $C_3H_6 + H_2O \rightarrow C_2H_4 + CO + 2H_2$

(III$_6$) $C_2H_4 + 2H + O_2 \rightarrow 2CO + 3H_2$

(IV$_6$) $CO + H_2O \leftrightarrow CO_2 + H_2$

(V$_6$) $H + H + M \rightarrow H_2 + M$

(VI$_6$) $O_2 + 3H_2 \leftrightarrow 2H_2O + 2H$

The consumption reactions for C_3H_6 and C_2H_4 are relatively slow compared to the four reactions of formation of them, which explains the relatively large concentrations of C_3H_6 and C_2H_4 found in rich flames. Therefore, these species cannot be assumed to be in steady-state for rich flames of propane.

3.1.5 Butane

To identify the main stages of the combustion of butane, we began by describing the thermal decomposition of this fuel resulting in *H* and C_4H_9. To obtain a reduced mechanism for butane, the species C_4H_9, C_2H_3, CH_3, C_4H_8O, *CHCO*, CH_2, *CHO* and

CH_2O are assumed to be in steady-state. Then, an 8-steps mechanism is obtained as follows:

(I$_8$) $C_4H_{10} + O_2 \rightarrow C_4H_7 + H + H_2O$

(II$_8$) $C_4H_7 \rightarrow C_3H_7 + CO$

(III$_8$) $C_3H_7 \rightarrow C_3H_6 + H$

(IV$_8$) $C_3H_6 + O_2 \rightarrow C_2H_2 + CO + OH + 3H$

(V$_8$) $C_2H_2 + O_2 + H_2 + OH \rightarrow 2CO + 2H_2O + 3H$

(VI$_8$) $CO + H_2O \leftrightarrow CO_2 + H_2$

(VII$_8$) $H + H + M \rightarrow H_2 + M$

(VIII$_8$) $O_2 + 3H_2 \leftrightarrow 2H_2O + 2H$

For large chains of hydrocarbons such as butane, the oxidation route via the isomers can be neglected, a fact also mentioned by Frolov et al (2006).

3.1.6 Pentane

To reduce the mechanism of pentane, it was considered the reaction of fuel with H of great importance, which leads to the production of C_5H_{11}. Other reactions of the fuel lead to insignificant production of C_4H_9, C_2H_5 and C_3H_7, so these species are discarded in the mechanism.

After assuming steady-state for the species C_5H_{11}, $C_5H_{11}O_2$, C_4H_9, C_4H_8, CH_3, CH_2, CHO and C_2H_2 it is obtained the 8-steps mechanism shown below:

(I$_8$) $C_5H_{12} + O_2 + H_2 \rightarrow C_4H_7 + CH_2O + H_2O + 3H$

(II$_8$) $C_4H_7 + O_2 + H_2 \rightarrow C_2H_4 + HCCO + H_2O + 2H$

(III$_8$) $C_2H_4 + O_2 \rightarrow HCCO + H_2O + H$

(IV$_8$) $HCCO + O_2 + 2H_2 \rightarrow CH_2O + CO + H_2O + H$

(V$_8$) $CH_2O \rightarrow CO + 2H$

(VI$_8$) $CO + H_2O \leftrightarrow CO_2 + H_2$

(VII$_8$) $H + H + M \rightarrow H_2 + M$

(VIII$_8$) $O_2 + 3H_2 \leftrightarrow 2H_2O + 2H$

Note that there are not C_3-chain species in the reduced mechanism of pentane. Besides, C_1 and C_2 species are notoriously important.

3.1.7 Hexane

In the reduction process of hexane it was found important the thermal decomposition of two isomers: C_6H_{13}-1, C_6H_{13}-3 and C_6H_{12}-3 in sequence. Then the process continues with the production of CH_3 and C_5H_9. Making the assumption of steady-state for the species C_6H_{13}-1, C_6H_{13}-3, C_5H_9, $C_3H_6OOH_1$-3, CHO, C_2H, $CHCO$, CH_3, OH and O it is obtained the 10-steps mechanism shown below:

(I$_8$) $C_6H_{14} + 2O_2 + 2H_2 \rightarrow C_2H_4 + C_2H_2 + 2CH_2O + 2H_2O + 4H$

(II$_8$) $C_2H_4 \rightarrow C_2H_2 + H_2$
(III$_8$) $C_2H_2 + O_2 + 2H_2 \rightarrow CH_2 + H_2O + H_2 + CO$
(IV$_8$) $CH_2O \rightarrow CO + 2H$
(V$_8$) $CH_2 + O_2 + H_2 \leftrightarrow CO + H_2O + 2H$
(VI$_8$) $CO + H_2O \leftrightarrow CO_2 + H_2$
(VII$_8$) $H + H + M \rightarrow H_2 + M$
(VIII$_8$) $O_2 + 3H_2 \leftrightarrow 2H_2O + 2H$

3.2 Numerical Results

In the following, a comparison of numerical values with experimental data found in the literature for Sandia Flame D (Barlow and Frank, 2003), for the mass fraction of CO_2, is presented. One uses the Flamelet equations for the species i, written for the mixture fraction Z as follows:

$$\frac{\partial Y_i}{\partial t} = \dot{w}_i + \frac{\chi}{2Le}\frac{\partial^2 Y_i}{\partial Z^2} \tag{3}$$

where w_i represents the rate of reaction of each species, χ the scalar dissipation rate, Z the mixture fraction and Le the number of Lewis.

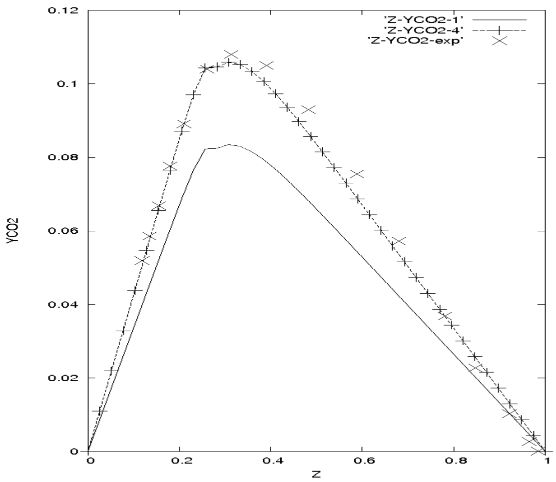

Figure 1: Comparison of CO_2 mass fraction in the mixture fraction space considering one and four steps for a flame of methane.

The mass fraction of CO_2, produced by the combustion of methane, is shown in Figure 1. The result from the four steps mechanism is in good agreement with the experiment. Therefore, the four steps mechanism describes adequately the combustion process for methane. For the other fuels the same behavior is expected.

4 CONCLUSIONS

This work presents a method to obtain reduced reaction mechanisms for the combustion of methane, acetylene, ethylene, propane, butane, pentane and hexane through the comparison of the specific rates of the elementary reactions and the use of the steady-state assumptions. The consistency of the global steps obtained is showed by the reactions of CO, H_2O, O_2, H and H_2, which appears for all hydrocarbons studied.

Note that as the chain increases, the number of steps tend to increase, i.e., the mechanism is composed of more species in non-steady-state. This indicates that the higher the hydrocarbon chain, more steps are needed to describe the combustion process without affecting its main chain.

We strong the fact that from the reduced mechanisms obtained it is possible to get one step mechanism with correct stoichiometry. The method developed to reduce mechanisms had been effective, because the intermediate species are in agreement with the works found in the literature. Moreover, this method leads to a satisfactory stoichiometry in the limit in which an one-step global mechanism is considered for each species. The comparison of the four steps mechanism with experimental data comproves it.

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