Methane combustion dynamics in a diabatic PSR with global, reduced and detailed reaction mechanisms

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1 Introduction

The understanding of combustion dynamics and of instability generation is a fundamental topic. Both theoretical and experimental studies highlighted the role of different mechanisms, like unmixedness of reactants [1], flame dynamics response to perturbations [2–4] and thermo-acoustic instabilities [5]. Nevertheless, quantitative predictions on the role of single mechanisms often lack a satisfactorily agreement. An incomplete knowledge of the effective behavior of the combustion kinetic under dynamic conditions is still present even if the possibility of a steadily oscillating combustion behaviour sustained by the sole kinetic is known from long time [6].

The role of a selected mechanism in the correct prediction of combustion dynamics need a better understanding too. Reduced chemical schemes are undoubtedly required when CFD simulations of reactive flows is pursued. Usually, the reduction of the chemical kinetics is performed in such a way that the reduced scheme is able at reproducing global parameters like the adiabatic temperature, the global burning rate or the laminar flame speed, rarely with a proper assessment of the ability to reproduce dynamical properties too [7,8].

In a previous work, the role of chemistry in determining the ability of a mixture to withstand perturbations in conditions close to extinction in a adiabatic PSR was investigated [9]. Several issues were highlighted about the ability of the global reaction to reproduce the behaviour obtained with the wellestablished GriMech 3.0 (GRI) scheme [10] for methane combustion. The PSR appears as the minimum archetype that allows to focus on the influence of the reaction mechanism on the description of the combustion phenomena.

In this work the PSR model is used to investigate the ability of two global and one reduced reaction mechanisms to reproduce the behavior of the reference kinetic scheme GRI, under dynamic conditions. Two main issue are addressed. The first is to enlarge the previous study to include a characterization of spontaneous oscillations, that can arise when a heat loss term is introduced. This is obtained by firstly

determining the bifurcation diagrams with the different mechanisms. Then, simulations are performed in key solution points where, spontaneously or by a proper forcing, periodic solutions are computed. Comparison of results allow to highlight several features on the dynamic response of the system and their dependences upon the selected mechanism.

2 Model Description and Methodologies

Perfectly Stirred Reactor The equations of time evolving non-adiabatic PSR can be written as [11]:

$$\frac{dY_j}{dt} = \frac{Y_{j,f} - Y_j}{\tau} + \frac{W_j r_j}{\rho V}, \quad j = 1, 2, \dots, N_s$$
(1)

$$\frac{dT}{dt} = \frac{\sum_{j=1}^{N_s} Y_{j,f}(h_{j,f} - h_j)}{c_p \tau} - \frac{\sum_{j=1}^{N_s} h_j W_j r_j}{\rho V c_p} - \frac{\alpha A(T - T_{env})}{\rho V c_p}$$
(2)

Here t, Y_j , τ , W_j , r_j , ρ , V, N_s , T, h, c_p , α , A refer to time, mass fraction of specie j, residence time, molecular weight of species j, molar reaction rate of species j, density, reactor volume, number of species, temperature, specific enthalpy, constant pressure specific heat, heat loss coefficient and surface area of the reactor respectively. The subscript f refers to reactor feeding (inlet) conditions and env to the environmental conditions. The residence time τ is defined as $\tau = (\rho V)/\dot{m}_f$ where \dot{m} is the mass flow rate.

Chemical models In this work we focus on methane-air combustion (air composition approximated as $O_2 21 \%$, $N_2 79 \%$ by volume). We will make use of a detailed kinetic schemes, a reduced mechanism and two different global reaction mechanisms: the Gas Research Institute 3.0 mechanism (GRI) [10]; the methane-air reduced mechanism by Lu and Law (LL) [12]; the 2S-CM2 global two-step mechanism [13]; the global one step mechanism by Westbrook and Dryer (WD) [14].

The Gas Research Institute mechanism, also known as GRIMech, is the most widely known chemical kinetics mechanism used for modelling methane and natural gas combustion in air. The current version (version 3.0) consists of 325 chemical reactions and 53 species. The LL reduced mechanism is obtained from GRIMech 3.0 by eliminating the unimportant species and reactions and by applying the directed relation graph method [15]. The reduction is based on reaction states sampled from auto-ignition and perfectly stirred reactor (PSR). The current version consists of 184 chemical reactions and 30 species. The 2S-CM2 mechanism is a two step global reaction mechanism developed in such a way that it is able to reproduce GRIMech 3.0 flame speeds for various equivalence ratios. Particularly, the authors of the mechanism show that results obtained with the 2S-CM2 are in a good agreement to that of detailed mechanisms for fresh mixture with T = 300 K, pressure p = 0.1 MPa and equivalence ratios between 0.6 and 1.0. The reactions and full specification of Arrhenius parameters are reported in table 1 (A, β , and E_a refer respectively to pre-exponential factor, temperature exponent, and Activation Energy of the Arrhenius law). The WD mechanism was developed by following a simple procedure. The authors set to zero the temperature exponent and they fix activation energy by using appropriate average between values found in scientific literature. Then held fixed the reaction orders, the pre-exponential factor was varied until the model correctly predicted the flame speed for an atmospheric pressure, stoichiometric fuel-air mixture. This procedure was repeated for different sets of reaction orders in order to find the set that correctly predicted the variation of flame speed with equivalence ratio. The reaction and full specification of Arrhenius parameters are reported in table 2. In this work was chosen the set 3 reported in the Westbrook and Dryer work in order to avoid negative reaction order. This set shows good (but not best) agreement between detailed mechanism and one-step mechanism [14].

Table 1: Reactions and Arrhenius parameters for 2S-CM2 mechanism [13] (units in cm, s, cal, and mol)

Tag	Reactions	A	β	E_a	Reaction Orders
2S-CM2-1	$CH_4 + 1.5O_2 \longrightarrow CO + 2H_2O$	2×10^{15}	0	35000	$[CH_4]^{0.9}[O_2]^{1.1}$
2S-CM2-2	$\text{CO} + 0.5\text{O}_2 \longrightarrow \text{CO}_2$	2×10^9	0	12000	$[CO][O_2]^{0.5}$
2S-CM2-2r	$CO_2 \longrightarrow CO + 0.5O_2$	8.1104×10^{10}	0	77194	[CO ₂]

Table 2:	Reaction	and Arrheniu	s parameters for	· Westbrook	and Dryer	mechanism	(units in	n cm, s	, cal
and mol)	[14]								

Tag	Reactions	A	β	E_a	Reaction Orders
WD	$CH_4 + 1.5O_2 \longrightarrow CO + 2H_2O$	2×10^{15}	0	35000	$[CH_4]^{0.9}[O_2]^{1.1}$

3 Results and Discussion

Bifurcation map In this work we limit the investigation by considering the residence time as the only continuation parameter. To construct the bifurcation diagram and identify the bifurcation points we use an homemade code. This code uses the pseudo-arclength continuation algorithm to compute the steady state solution curve and the *fold bifurcation test function* [16] to identify the bifurcation.

The bifurcation diagram for all the 4 mechanisms by varying the residence time is firstly shown. Conditions adopted are: stoichiometric mixture, atmospheric pressure and inlet temperature fixed to 1200 K. Heat transfer to the wall depends on $T_{env} = 300$ K and on the coefficient $\alpha A/V = 125.4$ W m⁻³ K. Several features are clearly identified. Bifurcation points are indicated by a circle symbol and labelled with a 2 to indicate limit points and with a 4 to indicate Hopf Bifurcations. Dotted lines indicate unstable branches. Ignition of the mixture, the first limit point encountered walking the curves from the lower values of τ , occurs at very different residence times, indicating the need to adopt the GRI or the LL mechanisms if ignition phenomena are investigated. Similarly, large differences are observed in the location of the second limit point, that identifies the extinction condition at low τ . The branches of ignited solution start from these different locations and are completely separated up to a residence time of about 1 s. The large temperature differences depends on the different heat of reaction produced by the schemes and the different number of species and final composition that lead to a different global specific heat. Thereafter, for higher residence times, heat losses comes into play, becoming the dominant phenomenon leading to the cooling of the mixture and eventually to the extinction. However, approaching this second critical conditions, a different behaviour spontaneously manifest, as before extinction periodic solutions arise starting from the Hopf Bifurcations points. The existence of periodic solutions before the last unstable branch is detected only with the GRI and LL mechanisms.

The behaviour of the reactor under natural dynamic conditions is illustrated in Figure 2. Simulations have been performed starting from conditions detected on the bifurcation diagram. Specifically initial conditions are fixed as those corresponding to the last Hopf Bifurcation of each mechanism. The residence times correspond to a shift of 0.01 s (solid lines) and 0.1 s (dashed lines) from these Bifurcation points. Noticeably, all mechanisms exhibits oscillations having frequency of the same order of magnitude, despite the different characteristic chemical time. Therefore, they are governed by a different characteristic times to be linked to the heat losses. The different dynamics emerges in the time required to reach periodic conditions and in the shape of the periodic oscillations. GRI and LL shows a period doubling moving from $\tau_{HB} + 0.01$ to $\tau_{HB} + 0.1$. Therefore the development of spontaneous peri-



Figure 1: Bifurcation diagram for the different reaction mechanisms.



Figure 2: Temperature oscillations for the different reaction mechanisms starting from steady conditions. All mechanisms compared on the left, inspection of GRI and LL on the rigth.

odic oscillations by the application of a disturbance in steady conditions could even be not recognized if, depending on the mechanism adopted, the simulation is not advanced enough in time. Even if the LL reduced mechanism performs very well in reproducing the behaviour of the GRI mechanism, some differences arises when looking at the frequencies, leading to a time lag between the two time signals.

A different dynamic behaviour can be detected in steady conditions by applying a periodic forcing. Following [1], the sinusoidal perturbation of the residence time $\tau(t) = \tau_0 [1 + \varepsilon \sin(2\pi ft)]$ was imposed to the inlet conditions of the PSR. The analysis is conducted at $\tau_0 = 0.001$ s and frequency of 1000 Hz) with a perturbation amplitude of 10%. Figure 3 illustrate the orbits obtained together with the baselines constituted by the steady solution branches (dash-dot lines). Both quantitative and qualitative differ-



Figure 3: Left: temperature orbits for the different reaction mechanisms starting from steady conditions. Right: temperature and methane mass fraction time signals.

ences arise. Oscillations with the detailed mechanisms (GRI and LL) have a much greater amplitude. Furthermore the slope of the main axis of the orbit is smaller than the corresponding slope of the tangent to the baseline bifurcation diagram in τ_0 for the GRI and LL mechanisms while it is greater for the reduced mechanisms. This can be explained by examining the phase shift between the temperature and methane mass fraction time signals. While T anticipate Y_{CH4} for the global mechanisms (only WD is shown in the figure for the sake of clarity), the contrary occurs for the detailed and reduced mechanisms (only GRI shown in the figure).

4 Conclusions

A comparison of the dynamic features of different chemical mechanisms for the methane combustion has been presented. Several conclusions can be withdrawn from the results:

- macroscopic, well known, differences arise in the bifurcation diagram in regions where chemical kinetics is predominant with respect to heat losses;

- the dynamic behaviour equally shows great differences among the several mechanisms: spontaneous periodic oscillations are reached in a longer time from application of the perturbation with the global mechanisms;

- periodic forcing of steady solutions can lead to oscillations with different qualitative properties when applied to the different mechanisms.

The proposed analysis contributes to a clearer interpretation on the dynamics of combustion.

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