

Non-linear response to periodic forcing of methane-air global and detailed kinetics in Perfectly Stirred Reactors

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1 General aspects

Environmental protection and energy saving are becoming the key issues that drive the further development of combustion technology. In this path the adoption of lean premixed or partially premixed (LPP) combustion appears an obliged route to reduce the emissions from gas turbine combustors. The shift from the diffusion to the LPP combustion regime is not straightforward: the possibility of occurrence of combustion instability has been widely reported in the literature [8] and promoted many studies to understand the mechanism of their generation. Both theoretical and experimental studies highlighted the role of different mechanisms, like unmixedness of reactants, flame dynamics response to perturbations and thermo-acoustic instabilities. Nevertheless, quantitative predictions on the role of single mechanism often lack a satisfactory agreement. Almost all studies share an incomplete knowledge of the effective behavior of the combustion kinetic under the action of perturbations of finite amplitude and frequency. This lackness is surprising in view of the fact that the possibility of a steadily oscillating combustion behavior sustained by the sole kinetic is known from long time [5] and that in almost any medium and large scale combustor, the combustion process is proficiency conducted in a turbulent, and therefore noisy, environment. Numerical simulation is a very useful approach for this problem because helps to isolate the possible causes for the occurrence of the instabilities while greatly reducing the cost of the study [2, 3]. 3D CFD (Computational Fluid Dynamics) simulations able to describe the unsteady structure of the flow (Large Eddy Simulation) can give clear insights in the phenomenon. However the necessity to include the full geometry of the combustor from feeding lines to the stack obliges to adopt reduced or simplified kinetic schemes to make affordable the computational effort. Usually, reduced kinetic schemes are selected on the basis of the ability to reproduce global parameters like the global burning rate or the laminar flame velocity, rarely with a proper assessment of the ability to reproduce dynamical properties too [12]. The inability to reproduce dynamical behavior is taken into consideration in the several numerical studies of flame ignition and quenching where the adoption of special tuning of the global reaction kinetic is unavoidable [6]. These observations promoted the present study.

Two main objectives are here pursued: firstly, to determine the extinction line in the $\phi - \tau$ plane, fixed the thermodynamic state conditions. Then, to characterize the response of the chemical system to periodic forcing of the state parameters in different points of the plane. In particular, we will select specific locations, some of them well inside the flammability region, while the others close to the extinction line. In addition, an assessment of the ability of different simplified chemical kinetic schemes to reproduce the behavior of a reference kinetic scheme (like the well-established GRI-Mech 3.0 scheme [11] for methane combustion), under the dynamic conditions due to the inlet perturbations, is proposed. In this work the response of a perfectly stirred reactor model to perturbations

of inlet flow conditions is presented. Transient simulations of combustion of methane with air, using both global single-step and detailed chemical kinetic mechanisms, have been conducted with imposed oscillation of mixture equivalence ratio and residence time around average values.

2 Numerical Model and Problem Setup

Unsteady perfectly stirred reactor. The perfectly stirred reactor (PSR) model is characterized by infinitely fast mixing and the characteristic times of motions are shorter than the chemical ones [13]. Therefore, in a PSR model perfect mixing is obtained instantaneously and the properties inside the combustor are uniform. The main advantage of using this kind of model is that the effects of chemical kinetics are isolated and can be considered in full detail. Of course it is far to represent a real system but useful general results can be derived by identifying the range of parameter values that mostly affect the dynamical response. The governing equations for the PSR model are expressed in the form suggested in [4]:

$$\frac{dM_i}{dt} = \dot{m}_{in} Y_{i,in} - \dot{m} Y_i + W_i V R_i, \quad i = 1, \dots, N_s \quad (1)$$

$$\frac{dU}{dt} = \dot{m}_{in} \sum_{i=1}^{N_s} Y_i h_{i,in} - \dot{m} \sum_{i=1}^{N_s} Y_i h_i - P \frac{dV}{dt} \quad (2)$$

A nominal and an effective residence time τ_{nom} and τ_{eff} can be defined respectively as:

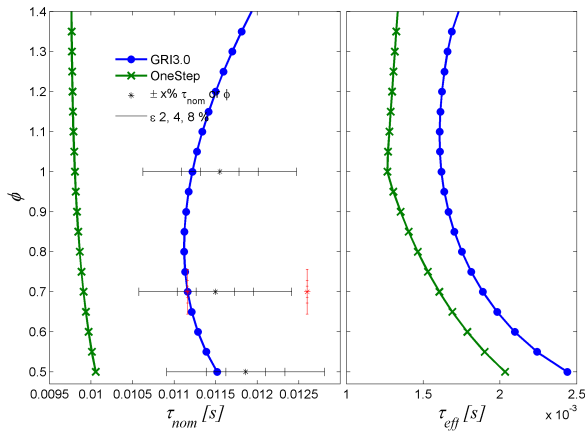
$$\tau_{nom} = \rho_{in} V / \dot{m}_{in} \quad , \quad \tau_{eff} = M_R / \dot{m} \quad (3)$$

Here t , y_i , ρ , h , Q , R_i , P , U refer to time, species mass fraction, density, specific enthalpy, heat transfer rate, species volumetric reaction rate, pressure and internal energy. The subscript *in* refers to conditions at the reactor inlet and $M_R = \sum_{i=1}^{N_s} M_i$ is the mass inside the reactor. No feedback was included in the PSR model: this open-loop response of the combustor to inlet flow variations implies that results are independent of the geometry-specific system dynamics. Numerical integration of these equations has been performed adopting the open-source CANTERA software library [4]. This library provides both routines for the efficient solution of large system of stiff ODEs and several interfaces that allows to setup the specific problem at handle in different programming environment ranging from low level languages (C++ and FORTRAN) to high level programming environments (Python and Matlab). The Python interface was used in this study.

Chemical models. The chemistry of methane-air has been modeled by a global single-step and a detailed finite-rate mechanism. The global single step has been proposed by [9] to study the dynamical behavior of a PSR working in conditions representative of a gas turbine combustion chamber. For the latter, the GRI-Mech 3.0 [11] was used. This mechanism comprises 325 elementary reactions and 53 species.

3 Determination of the extinction line

PSRs are often employed as a extremely simplified representation of real devices. Nevertheless, as often happens when oversimplifications are adopted to get a simpler mathematical model, the awareness of the implicitly introduced hypotheses have to be considered. In Figure 1 the behaviour of the extinction line in the $\tau_{nom} - \phi$ (left) and $\tau_{eff} - \phi$ planes are reported for both the chemical mechanisms adopted. Also indicated are the points where successive computations with forced inlets will be performed. Firstly, it is clearly observed the need to correctly deduct the proper stability limits with respect to the residence time definition: when estimate is done with respect to τ_{nom} , further effects couple with the residence time, as the non linear dependence of the temperature upon stoichiometry, and therefore of the volume expansion ratio, that are instead implicitly included in the definition of τ_{eff} .



ϕ	$0.5 \leq \phi \leq 1.0$	[-]
$\bar{\tau}_{nom}$	$0.009 \leq \bar{\tau}_{nom} \leq 0.04$	[s]
ε (%)	$\varepsilon = \{2, 4, 8\}$	[%]
f	$1 \leq f \leq 1600$	Hz

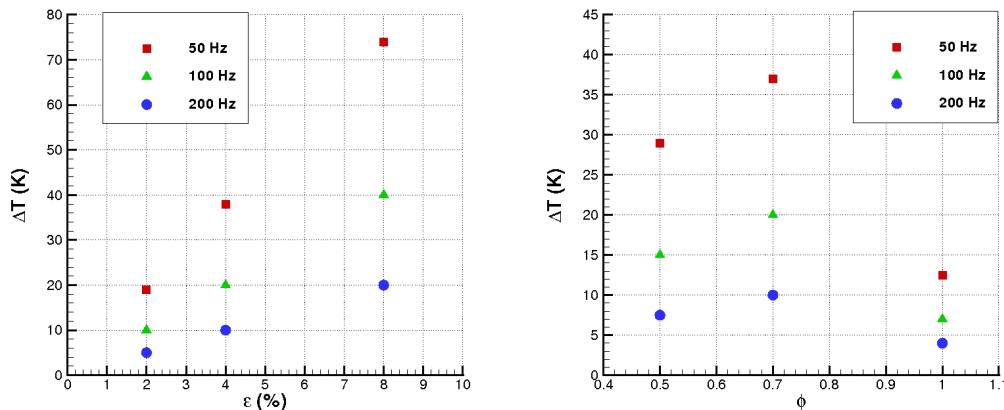
Table 1: Free parameters variation.

Figure 1: Limiting curves of ignited states in the $\tau - \phi$ plane: versus τ_{nom} on left, versus τ_{eff} on right.

4 Analysis of dynamic behavior under periodic forcing

Following the studies of [9] and [7], simulations with periodic variations of the PSR inlet were performed. In particular, the attention has been focused on the response of the system to a sinusoidal perturbation of the equivalence ratio and of the residence time. When the equivalence ratio is varied, the total inlet mass flow is not changed, in order to keep constant the residence time. The free parameters are the average value of the perturbed variable, the amplitude and the frequency of the perturbation. The equivalence ratio has been varied according to the expression $\phi(t) = \bar{\phi}[1 + \varepsilon \cos(2\pi ft)]$. The free parameters are varied according to the values reported in table 1. Attention has been focused on the range of lean mixtures ($0.5 < \phi < 1$).

Frequency and Amplitude of Perturbation. Figure 2 (left) shows the amplitude of the temperature variation as a function of the amplitude of the inlet perturbation at different frequencies and for an average equivalence ratio of 0.7. It can be seen that the response increases linearly with the increase of the perturbation amplitude,

Figure 2: PSR response for a periodic forcing of the inlet equivalence ratio in terms or temperature: effect of perturbation amplitude at various frequencies (left) and $\bar{\phi} = 0.7$; effect of $\bar{\phi} = 0.7$ at various frequencies and $\varepsilon = 4\%$.

while it decreases with the increase of the frequency. Figure 2 (right) shows the variation of the amplitude of the average temperature as a function of the average equivalence ratio, for various frequencies at an amplitude of $\Delta\phi_{in} = 4\%$. The response of the temperature increases with ϕ , it reaches a maximum at $\phi = 0.7$ and then decreases. This result shows that the system has an increased response to the perturbation in the lean range

far from limiting conditions. Correspondingly, three type of dynamic behavior can be identified: the first, in the very lean limit, is characterized by small amplitude response to perturbations but extinction and re-ignition mechanisms can easily couple raising the amplitude of the response. The second, far from limiting values of lean stoichiometry, are characterized by the highest amplitude of the response: in this range both the minimum and maximum value of the perturbation correspond to value of minimum and maximum of the burning rate. The third, close to stoichiometric conditions, is characterized by a one-side response of the burning rate, already at its maximum value for the average condition. Figure 3 (left) shows the temperature amplitude variation with frequency for all the average $\bar{\phi}$ considered. Note that in this picture the amplitude has been normalized with its maximum. A first observation is that the system behaves like a low-pass filter, and that the cut-off frequency is below 100 Hz (considering a decay of $1/e$ in the temperature amplitude). This value is well comparable with

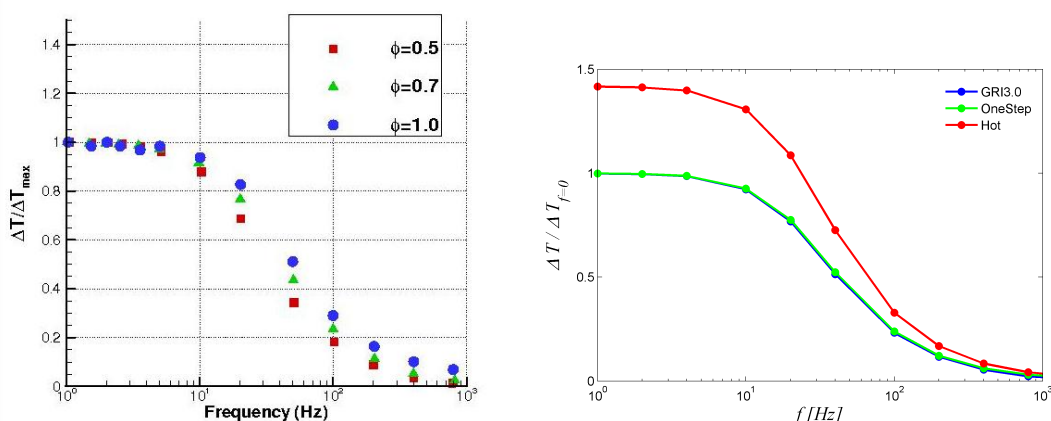


Figure 3: Normalized PSR response for a periodic forcing of the inlet equivalence ratio in terms of temperature: effect of perturbation amplitude at various frequencies (left) and $\bar{\phi} = 0.7$; effect of kinetic mechanism at $\bar{\phi} = 0.7$ and $\epsilon = 4\%$ versus frequency ..

the characteristic values of thermoacoustic oscillations experimentally observed in real gas turbine combustor [8], raising the issue of a possible role of the kinetic in their occurrence and stabilization. As a matter of fact, the addition of small quantities of hydrogen in the blend of reactant species, that leads to a change of the reaction path, greatly impact on the stability characteristic of LPP combustors [10]. Furthermore it is interesting to note the similar behavior of amplitude decay with frequency observed in experimentally measured flame transfer function by [1].

In order to correctly capture the flame dynamics by means of Computational Fluid Dynamics simulations, it is necessary that the described response to perturbations is correctly reproduced by adopting a reduced kinetic scheme. The same analysis has been therefore conducted with a global single-step reaction mechanism by [9]. Results both in terms of amplitude of temperature and effective residence time oscillations are qualitatively unchanged when using the global single-step mechanism (not shown) far from limiting equivalence ratio. The two mechanisms behave differently when their response to perturbations are compared close to limiting conditions. In Figure 4 the two responses are compared varying the frequency at $\bar{\phi} = 1$ and $\epsilon = 4\%$. While the temperature pattern remains similar (4, left), significant discrepancies (4, right) are observed for the effective residence time (nominal residence time being obviously coincident). The observed inversion of the behavior is really significant being the residence time one of the parameters mostly influencing the dynamic response of real combustors.

Nevertheless it has to be remarked that, because of the infinitely fast mixing hypothesis in a PSR model, this model inherently smooths all signals having higher frequency. Therefore the observed damping of the oscillations at higher frequencies have to be compared with the characteristic damping properties of the PSR before to conclude that have to be related with the characteristic time of the chemical kinetic. Such a comparison is proposed in figure 3 (right) where the comparison is made with a non reactive flow entering into the PSR and heated by the amount required to reach, in steady conditions, the same outlet temperature of the burning mixture. As expected trends are similar but not identical, highlighting the effective role of the chemical kinetics in establishing the behaviour of the system subject to periodic forcing. The response of the system to forced oscillations is effectively observed

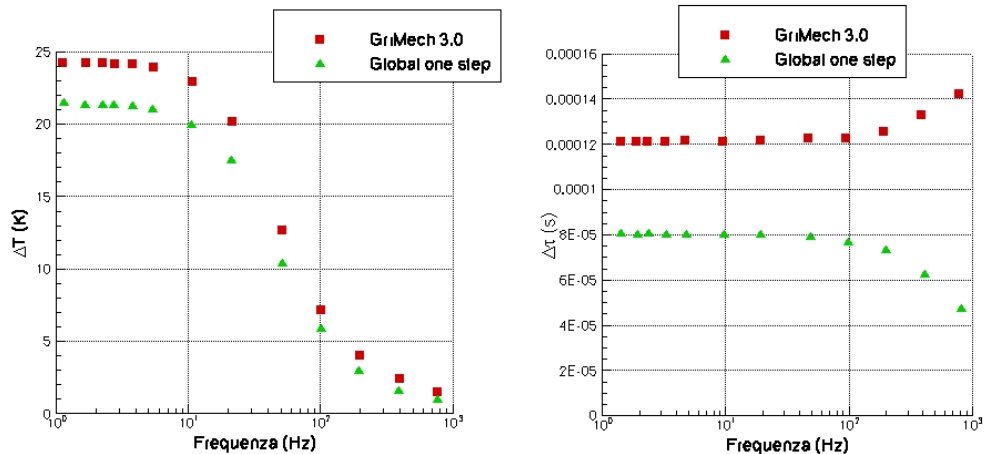


Figure 4: Amplitude of temperature (left) and effective residence time (right) response versus frequency: red symbols GriMech 3.0, green symbols global one-step. $\bar{\phi} = 1$, $\epsilon = 4\%$.

at lowest frequencies while it is hidden at higher frequencies by the PSR behaviour.

Phase Shift Analysis. Another important aspect to analyze is the phase shift of the various species with respect to the equivalence ratio variation as a function of the frequency. This aspect is indeed important in the analysis of the formation of pollutant species by means of numerical simulation with the reduced chemical mechanisms usually adopted in CFD simulations. Furthermore phase shift is a key parameter in the establishing of the conditions that rule combustion instabilities as stated by the Rayleigh criterion. Results are reported for three selected frequencies: 5 Hz, 50 Hz, 400 Hz. Attention is focused on CH₄ (reactant), CO₂ (product) and OH (intermediate). Also the temperature has been reported. Figure 5 shows the phase shift for the various species and temperature for

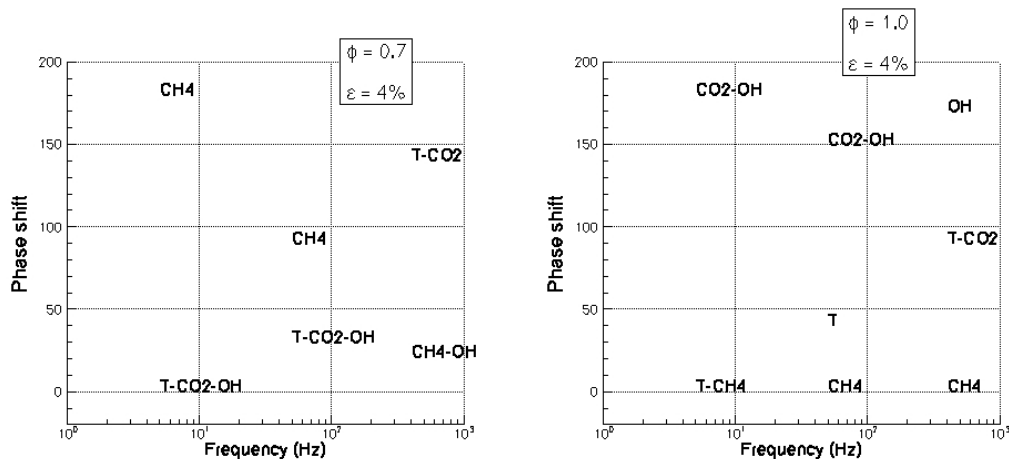


Figure 5: Phase shift of oscillations of major species and temperature versus frequency computed with the GriMech 3.0 at $\bar{\phi} = 0.7$ (left) and $\bar{\phi} = 1$ (right), $\epsilon = 4\%$.

equivalence ratio of 0.7 (left) and 1.0 (right). Let's us first consider the case for $\bar{\phi} = 0.7$. The reactant CH₄ is in opposite phase at low frequency, while increasing f it reduces its phase shift until it is in phase at high frequency. The product CO₂ and the temperature have an opposite behavior with respect to methane: they are in phase at low frequencies and becomes delayed at high frequencies. Therefore when the temperature is higher, also the methane consumption is higher. The intermediate species OH instead has a little phase shift for all the frequencies analyzed. At the $\bar{\phi} = 1$ the behavior of the system changes. The methane is always in phase with the mixture fraction variation. CO₂ and temperature have no more the same behavior. CO₂ is in opposite phase at low frequencies and reduces its phase shift at higher frequencies. The temperature instead is in phase at low frequencies and then

increases its phase shift. Finally OH species is now nearly in opposite phase for the frequencies analyzed. When using the global one step mechanism at $\bar{\phi} = 1$ the species behavior change: the temperature, CO₂ and CH₄ have the same phase shift, which is zero at low frequencies and then increases at higher frequencies. Therefore the global one step mechanism is not able to capture the correct phase response of the system.

4 Conclusions

Several other effects have been analyzed but here not reported for brevity: they include the effect of the residence time oscillations and the behavior in limiting conditions. All these results show that in many conditions the adopted global mechanism is not able at reproducing the dynamic behavior obtained with the GriMech detailed mechanism, often either qualitatively. The comparison of the behavior of several global mechanism and a deeper analysis of the observed behavior will be conducted to identify the minimum requirements that simplified mechanism have to satisfy in order to successfully substitute detailed mechanisms without compromising the accuracy of results.

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