NON-LINEAR RESPONSE TO PERIODIC FORCING OF METHANE-AIR IN CONTINUOUS STIRRED TANK REACTORS

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Abstract
This paper focus on the study of the behavior of a continuous stirred tank reactor (CSTR) under the action of perturbations of finite amplitude and frequency. Two main objectives are here pursued: to determine the extinction line in the equivalence ratio (φ) – residence time (τ) plane, fixed the thermodynamic state conditions; and to characterize the response of the chemical system to periodic forcing of the state parameters.
Transient simulations of combustion of methane with air, using both global single-step and detailed chemical kinetic mechanisms, have been conducted. Results indicate very different dynamical behaviors, posing the issue of a proper choice of the kinetic scheme for the numerical study of combustion oscillations.

Introduction
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. This technology often will couple with the adoption of new fuels produced from renewable sources, like biofuels [**1**]. Therefore a large effort in developing new chemical kinetic schemes is running, posing new questions about their behavior when included, in full or simplified form, in simple or complex models of combustors.
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 [**2**]. 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 [**3**]. These observations promoted the present study.

Mathematical Model
The Continuous Stirred Tank Reactor (CSTR) model is adopted giving a set of non-linear ordinary differential equations (ODEs); for equations refer to [**4**]. No

feedback was included in the CSTR model: this open-loop response of the reactor to inlet flow variations implies that results are independent of the geometry-specific system dynamics. Model is closed assuming the ideal gas law, the chemical model and the thermodynamic data. A well posed problem is obtained by specifying initial conditions, feeding concentration of species, volumetric flow rate. All these information are summarized in Table 1. Numerical integration has been performed adopting the open-source CANTERA software library [**9**].

Table 1. Initial conditions, feeding concentration of species, volumetric flow rate, chemical model and thermodynamic data

Initial Condition	Reactor was filled only with N_2
	$P = 1$ atm
	$T = 300$ K
Volumetric Flow Rate	$Q_{f,Fuel} = \frac{\theta}{\rho_f}\,\varphi\,W_{Fuel}$
	$Q_{f,Air} = \frac{\theta}{\rho_f}\,4.7619\left(x+\frac{y}{4}\right)W_{Air}$
	$Q = \frac{1}{\rho}\left(\rho_f\,Q_{f,Air} + K_v(P - P_{env})\right)$
Chemical Models	GriMech 3.0 [**5**] (GM3)
	Lilleberg et al. [**6**] (LIL)
	Mantel et al. [**7**] (MAN)
Thermodynamic Data	NASA polynomial thermodynamic data [**8**]

Determination of the extinction line

The extinction line is the line in the plane $\varphi - \tau$ which identifies the limiting conditions for the extinction of the fuel-oxidizer mixture. They are identified through numerical simulations, performed using a bisection method: search of the limiting nominal residence time ($\tau_{nom,lim}$) is started from a condition of ignited mixture and one for which extinction occurs, so that they bracket the extinction condition. Simulations in the test conditions are always started from ignited initial conditions, keeping constant the equivalence ratio.

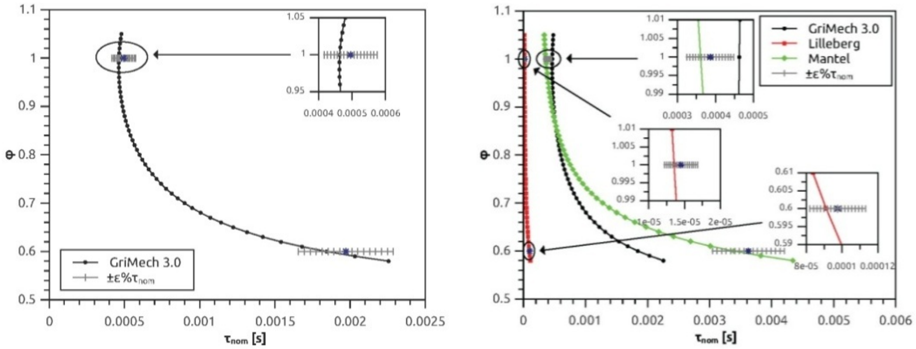

Figure 1. Extinction lines for the three mechanisms adopted.

The comparison of the extinction lines obtained with the different mechanisms is reported in Figure 1. The extinction curve obtained by adopting LIL is located at residence times an order of magnitude lower than the extinction curve of GM3. Instead the extinction curve of MAN is comparable with the extinction curve of GM3. This is due to difference in the overall reaction order: the overall reaction order of LIL is 2 (1 respect to methane and 1 respect to oxygen) while the overall reaction order of MAN is 3 (1 respect to methane and 2 respect to oxygen). The inset magnifications show in detail the regions that will be further investigated in this work. Focused is on mixtures with equivalence ratio $\varphi = 0.6$ and *1*.

Table 2. Simulations test conditions.

		Data	Units
(φ, τ_{nom})	GM3	{(0.6; 1.97092); (1.0; 0.49526) }	(-, ms)
	LIL	{(0.6; 0.097545); (1.0; 0.014492)}	
	MAN	{(0.6; 3.6234); (1.0; 0.386217)}	
ε		{2; 4; 6; 8; 10; 12; 14; 16}	%
f		{1; 10; 100; 200; 400; 600; 800; 1000; 1200; 1400; 1600; 1800; 2000; 2500; 3000; 3500; 4000; 4500; 5000; 5500; 6000}	Hz

Following [**10**] [**6**], simulations with periodic variations of the CSTR inlet were performed. In particular, the attention has been focused on the response of the system to a sinusoidal perturbation of the residence time. Residence time has been varied according to the expression $\tau_{nom} = \bar{\tau}_{nom}\,(1 + \varepsilon\, \cos(2\pi f t))$; where $\bar{\tau}_{nom}$ is taken 7% greater than $\tau_{nom,lim}$. Therefore, when applying an amplitude of the perturbation less than 7% , the reactor fully evolve inside the ignited region and no extinction can be observed. On the contrary, when an amplitude of the perturbation greater than 7% is applied, it could be possible to get the extinction of the mixture. All the test conditions investigated are specified in Table 2.

Frequency and Amplitude Response to Perturbations

For each pair $\varphi - \tau_{nom}$, the minimum frequency, among those considered, needed to support combustion conditions with the increase of the amplitude of the perturbation is firstly identified (see Figure 2). It results that with the increase of the equivalence ratio an increasingly high frequency is required to support combustion at constant amplitude of the disturbance. In this figure the extinction map for the LIL is not reported because this map consists of a single point (8%, 3000 Hz) in the frequency range analyzed. Results indicate that a stoichiometric mixture in conditions close to extinction is weaker than a lean mixture when subject to perturbations of the residence time, in the sense that it is necessary to increase the frequency to sustain the reaction for a given value of the amplitude of the oscillation with respect to a leaner mixture.

The system behavior varying the frequency of the perturbation can be described in terms of a dimensionless amplitude of temperature response. The reference temperature is assumed to be the reactor temperature without disturbance at the same condition with disturbance, and it is indicated with T_{steady}.

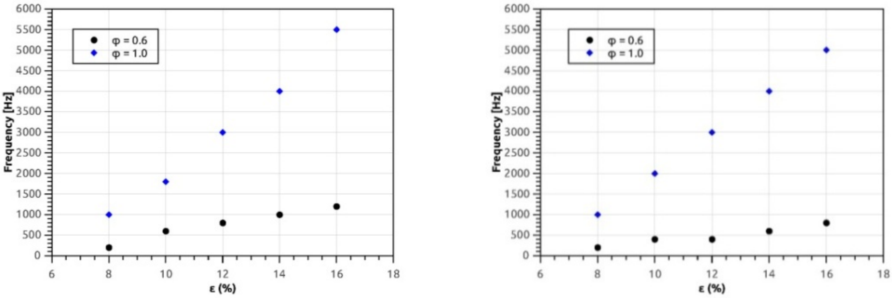

Figure 2. Limiting ignited conditions in the ε-f plane. From left to right: GriMech3.0 and mechanisms.

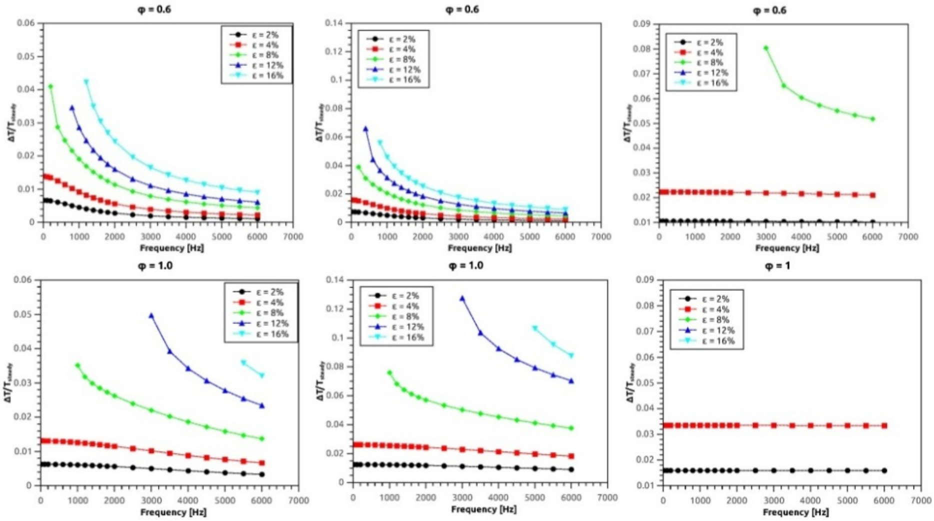

Figure 3. Dimensionless amplitude of temperature response versus frequency at different ε. From left to right: GriMech3.0, Mantel and Lilleberg mechanisms.

Corresponding results are reported in Figure 3, that makes evident that LIL is almost not sensitive to the frequency in the spanned range of parameters. Instead GM3 and MAN have similar behavior. As expected, by increasing the amplitude of the disturbance, increases the amplitude of the temperature response. Furthermore it is quite evident that the frequency has a stabilizing effect on the system by reducing the amplitude of the response to the perturbation. The trends of amplitude of temperature response to changes in equivalence ratio shows that by increasing the equivalence ratio, the system becomes less and less sensitive to the frequency of the perturbation. Thus, the temperature variation reached during the cycle with respect to the temperature of the unperturbed system is maximum at stoichiometric conditions. From Figure 3, it is recognized the interplay between the residence time and the mixing time, this last assumed to be null in the CSTR hypothesis: when the period of the oscillation is increased behind the residence time, the instantaneous mixing avoid the possibility to effectively burn a mixture in conditions corresponding to those of the instantaneous inlet conditions because, due to the instantaneous mixing, the reactor sees inlet conditions approaching to their average. The chemical time of leaner mixtures is slower, and therefore they are more affected by a longer period of the oscillation, practically acting as a low-pass filter for high frequency oscillations.

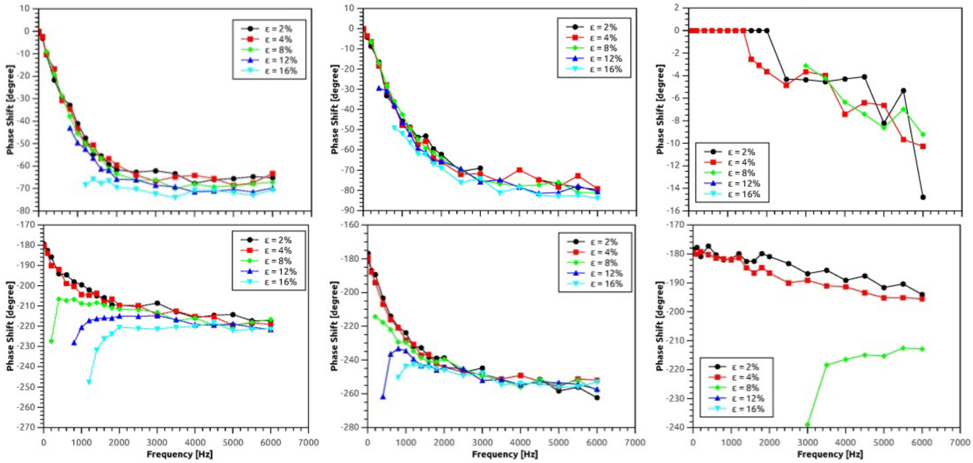

Figure 4. Phase shift of T (top) and CH_4 (bottom) versus frequency at $\varphi = 0.6$. From left to right: GriMech3.0, Mantel and Lilleberg mechanisms.

Phase Shift Analysis

The phase, reported for the temperature and the molar fractions of methane in Figure 4, is computed taking the difference between the time of maximum value of the reference nominal residence time signal, and the time of maximum of the output of the system. Not ignited conditions are not shown. A general trend is observed: increasing the frequency, also the phase shift is increased. This can be easily correlated to the fact that at the highest frequencies the period of the oscillations becomes comparable with the characteristic chemical time scale. The phase shift appears not affected significantly by the amplitude of perturbation in conditions far from extinction. When extinction conditions are approached, the perturbation amplitude have a strong effect on the phase shift of the CH_4 signal. The phase shift of LIL proves to be not significantly sensitive to the frequency.

Conclusions

Several other system quantities have been analyzed but here not reported for brevity. All the results led to two conclusion. Firstly it is clearly recognized that the CSTR behavior is similar to a low pass filter. The “cutoff frequency” is linked to the chemical time, proportional to the residence time at extinction, and therefore to the equivalence ratio. The results underline the role of chemical kinetic mechanism. Not all the adopted global mechanisms was able at reproducing the dynamic behavior obtained with the GM3, 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 in simulations of dynamical combustion systems.

Nomenclature

K_v	arbitrary constant	ε	amplitude of perturbation
f	frequency of perturbation	θ	proportionality constant ($\theta = V_R/\tau_{nom}Q_f$)
P	pressure	ρ	density
Q	volumetric flow rate	τ_{nom}	nominal residence time ($\tau_{nom} = Q_f/V_R$)
T	temperature	τ_{eff}	effective residence time ($\tau_{eff} = Q/V_R$)
t	time	φ	equivalence ratio
W	molecular weight	**Subscripts**	
V_R	reactor volume	*env*	environment
x	number of carbon atoms	*f*	feeding conditions
y	number of hydrogen atoms	*lim*	limit conditions

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