

Effect of Chemical Kinetics and Heat Transfer in the Dynamics of MILD Hydrogen Combustion

L. Acampora, M. Lubrano Lavadera, P. Sabia, R. Ragucci, M. de Joannon, F. S. Marra

Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy

Introduction

This contribution reports about results obtained, both experimentally and numerically, in the dynamic regime of a Jet Stirred Flow Reactor (JSFR) fueled with hydrogen and operated under MILD conditions for operating parameters values at which dynamic regimes occur.

It is shown that mixtures of hydrogen and oxygen diluted in nitrogen and argon at different inlet temperatures exhibit a dynamic behavior at a specific range of relatively low inlet temperature, just after the start of the combustion process.

Numerical simulations in a non-adiabatic Perfectly Stirred Reactor (PSR), conducted using a new tool for the parametric continuation of detailed chemical mechanisms, are used to verify the ability of present detailed chemical mechanisms of hydrogen combustion to reproduce the observed behavior both in terms of the temperature rise and in the ability to correctly detect the extent of the region of stable dynamic (periodic regime) combustion.

Through the comparison of experimental and numerical maps of solutions, current uncertainties still present even for this simple fuel and its oxidation process at low temperature are highlighted.

Experimental setup

Experiments were carried out in a spherical quartz Jet-Stirred Flow Reactor of $1.13 \times 10^{-4} \text{ m}^3$ electrically heated. Hydrogen, oxygen and diluent are each drawn separately from cylinders. Precise control of gaseous flow rates is achieved by means of thermal mass flow controllers upstream of the vessel, which are preceded by filters to retain particulate impurities. The reactants are pre-heated separately before flowing into the vessel. Inlet temperature (T_{in}), pressure (P), residence time (τ), and the reactant mixture composition define the control parameters. The reactant pressure is kept constant by means of a needle valve located on the gas exhaust line.

Data acquisition allows to measure inlet and reactor temperature and pressure with a combined response time for the sampling system and the acquisition of roughly 0.03 s. Record of mass flow rate in feeding lines and molecular products compositions during the reaction is realized. Maximum relative errors in mole fractions are estimated to be $\pm 10 \%$ when the concentrations approach the detection threshold (about 10 ppm).

The tests are conducted from initial conditions corresponding to the desired operating pressure, temperature and residence time up to the establishing of thermal equilibrium before any further change of parameters to characterize extents of self-heating correctly at the fixed temperature. Each result is referred to the set pressure, residence time and temperature established prior to reaction taking place. Therefore, the inlet temperature has not been varied continuously, but each experimental point corresponds to a different test.

Mathematical Models

The JSFR is modelled as an ideally PSR, whose equations can be given as:

$$\begin{aligned}\frac{dY_i}{dt} &= \frac{Y_{i,f} - Y_i}{\tau} + \frac{W_i r_i}{\rho}, \quad i = 1, \dots, N_S \\ \frac{dT}{dt} &= \sum_{i=1}^{N_S} \frac{Y_{i,f}(h_{i,f} - h_i)}{\tau c_p} - \sum_{i=1}^{N_S} \frac{W_i r_i h_i}{\rho c_p} - \frac{Q}{\rho V}\end{aligned}\quad (1)$$

Here t , ρ , T , N_S , c_p refer to time, gas density, temperature, number of species, and mixture constant pressure specific heat, respectively. Y_i , W_i , r_i , and h_i , are the mass fraction, molecular weight, net species production rate and specific enthalpy of the i -th species; the subscript f indicates the feeding (inlet) conditions, $\tau = \rho V / \dot{m}_f$ is the nominal residence time related to the reactor volume (V) and the mass flow rate (\dot{m}_f) and $Q = UA(T - T_{env})$ represents the Newtonian-type reactor heat loss depending on global heat transfer coefficient (U), reactor surface (A) and environmental temperature (the temperature of the ovens, T_{env}).

The heat transfer correlation for spherical geometry developed by Lignola and Reverchon [1] is adopted in this work:

$$U = 0.89 \text{Re}_N^{0.683} \text{Pr}^{1/3} \frac{k}{D} \quad (2)$$

where k is the thermal conductivity of the gas mixture, D is the reactor internal diameter and $\text{Pr} = \mu c_p / k$ is the Prandtl number (μ is the dynamic viscosity). In this work, it was assumed that two of the contributions considered in [1], the oven side thermal resistance and the thermal resistance of reactor wall, can be neglected. Therefore, only the reactor side heat transfer coefficient is taken into account.

Three different reaction schemes are adopted to model hydrogen oxidation: the detailed combustion of H_2/O_2 mixtures introduced by Ó Conaire et al. [2]; the optimized kinetic model of H_2/CO combustion proposed by Davis et al. [3]; the detailed mechanism for hydrogen oxidation developed by Politecnico di Milano [4, 5]. Different mechanisms are taken into account in order to isolate the effects depending on heat transfer from those depending on kinetic phenomena.

The numerical analysis is performed by using the parametric continuation tool introduced in [6, 7] and considering the feed mixture temperature as continuation parameter.

Results

Fig. 1 reports the temperature increment in the reactor and dry mole fractions of H_2 and O_2 versus temperature of a lean (equivalence ratio $\phi = 0.5$) hydrogen/oxygen/nitrogen (3%/3%/94% by volume) mixture at 121590 Pa (1.2 atm) burning in the JSFR with $\tau = 0.5$ s.

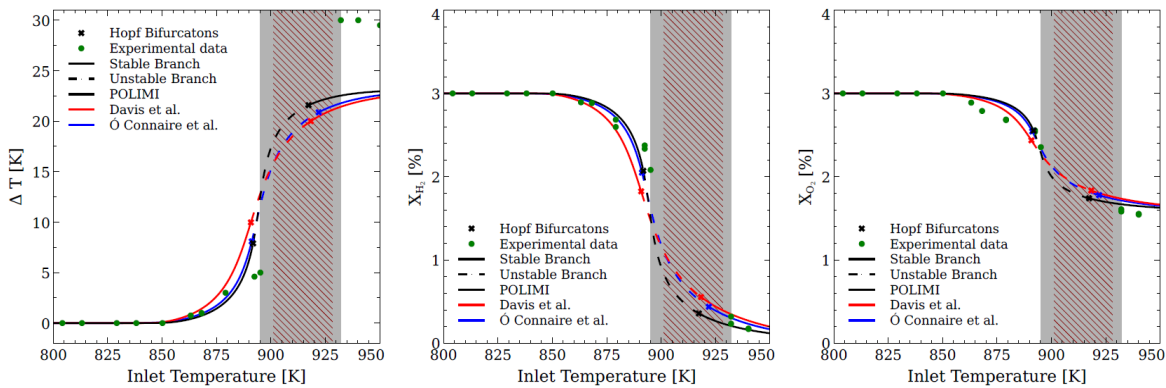


Figure 1. Temperature increment and dry mole fractions of H_2 and O_2 versus temperature with nitrogen diluent.

The experimental data are compared with numerical results obtained using the three different reaction mechanisms. The dashed lines identify the unstable branches. The shaded region

identifies the zone where sustained oscillations may be experimentally found. The forward diagonal lines highlight the zone where oscillatory behavior is experimentally found. Several discrepancies are detected. Even if the three mechanisms considered qualitatively reproduce the experimental results, none of these is able to quantitative reproduce the temperature increment in the reactor both before and after the unstable branch. Furthermore, none of these mechanisms appear to predict correctly the extent of the region where sustained oscillations are experimentally detected. Indeed, the position of the Hopf bifurcations, regardless of whether they are sub- or supercritical, cannot explain the observed region of oscillations. However, the predicted mole fractions appear to be consistent with the experimental results (percentage errors lower than 8%).

Similar results are found also adopting a different diluent like argon. Figure 2 show the same variables versus inlet temperature but adopting a lean mixture (equivalence ratio $\phi = 0.443$) of hydrogen/oxygen/argon (2.584%/2.916% /94.5% by volume) at 111457 Pa (1.1 atm) with residence time of $\tau = 0.46$ s.

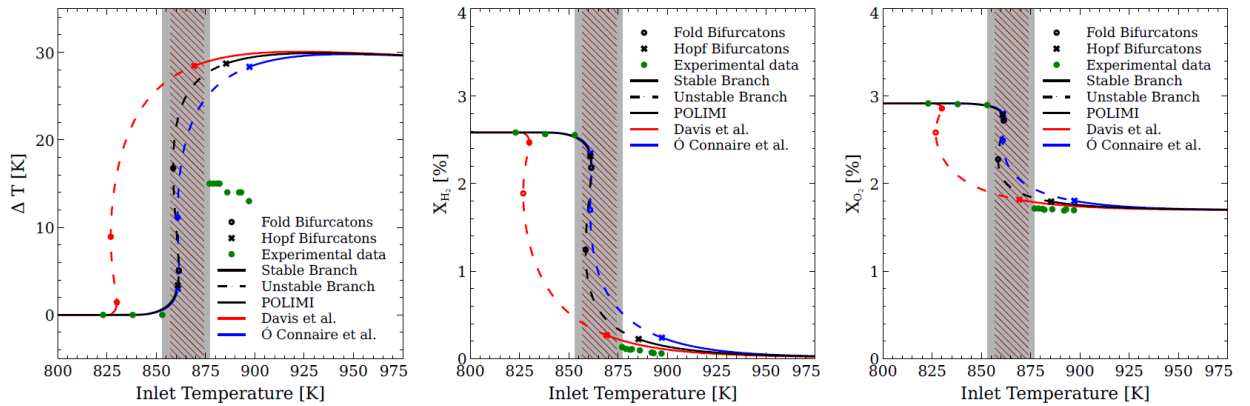


Figure 2. Temperature increment and dry mole fractions of H_2 and O_2 versus temperature with argon diluent.

These results confirm that none of the three mechanisms considered is able to reproduce the temperature increment in the reactor (this increment is now overestimated) and the extent of region where sustained oscillations are experimentally detected. Furthermore, the comparison between the three mechanisms shows that the mechanism proposed by Davis et al. is significantly different from the others.

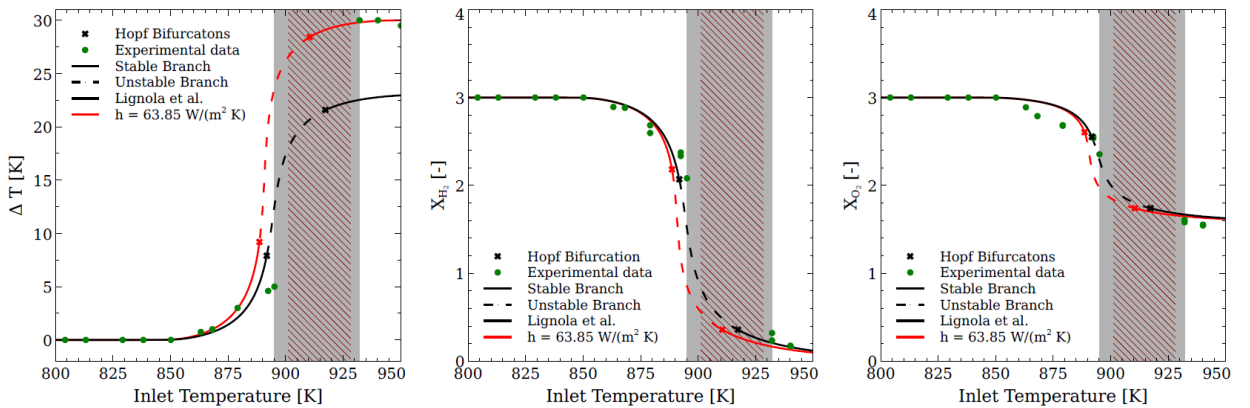


Figure 3. Temperature increment and dry mole fractions of H_2 and O_2 versus temperature with nitrogen diluent and tuned U .

Single point matching between experimental and numerical results can be easily achieved by tuning of the main model parameters. However, the investigation of the maps of solution allowed by parametric continuation, permits to verify the effectiveness of the new tuned

parameter values. The circumstance that the major discrepancies arise in the value of temperature increment suggests that the estimate of heat transfer at the wall could be affected by error. Therefore, the parameter U has been tuned to obtain a match with the experimental data in the point of maximum error between experiments and numerical simulations. Results are collected in Figures 3 and 4.

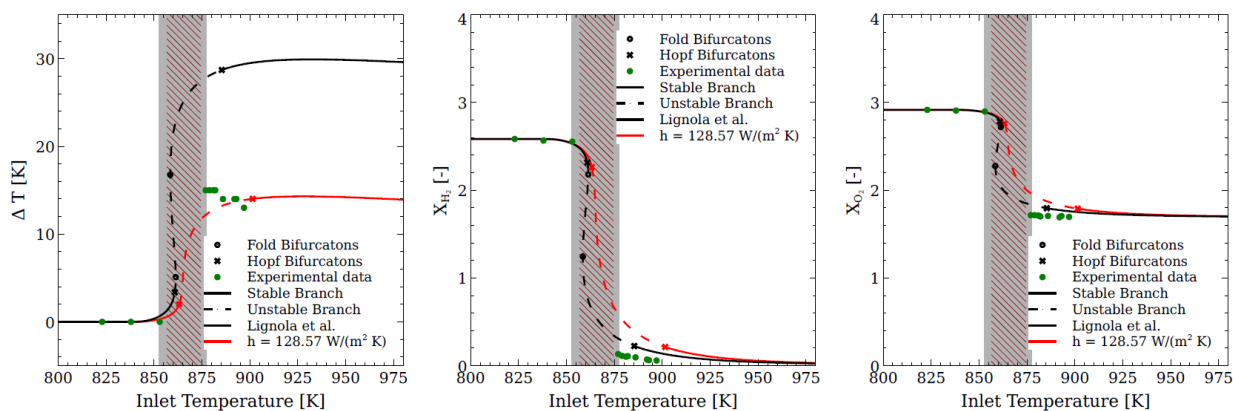


Figure 4. Temperature increment and dry mole fractions of H_2 and O_2 versus temperature with argon diluent and tuned U .

It results that the correction of the parameter U leads, apart from a corrected prediction of the temperature increment, to a worse prediction of the dynamic features of the process, with the shift of the Hopf bifurcations to lower values of inlet mixture temperature and disappearance of the two Fold bifurcations now replaced by a Hopf bifurcation and the beginning of the stable ignited branch.

Conclusions

The differences between numerical and experimental data suggest the need to update the reaction mechanisms for a better prediction of the combustion features under MILD conditions, especially in presence of different bath gases. The effectiveness of adopting a parametric continuation tool in the analysis of detailed chemical mechanisms is also demonstrated.

References

- [1] P. G. Lignola, E. Reverchon, Comb. Sci. Tech. 60 (1988) 319–333.
- [2] M. Ó Conaire, H. J. Curran, J. M. Simmie, W. J. Pitz, C. K. Westbrook, Int. J. Chem. Kin. 36 (2004) 603–622.
- [3] S. G. Davis, A. V. Joshi, H. Wang, F. Egolfopoulos, , Proc. Comb. Inst. 30 (2005) 1283–1292.
- [4] A. Frassoldati, T. Faravelli, E. Ranzi, Int. J. Hydrogen En. 32 (2007) 3471–3485.
- [5] A. Cuoci, A. Frassoldati, G. Buzzi Ferraris, T. Faravelli, E. Ranzi, Int. J. Hydrogen En. 32 (2007) 3486–3500.
- [6] L. Acampora, E. Mancusi, F. S. Marra, Chem. Eng. Trans. 43 (2015) 877–882.
- [7] L. Acampora, F. S. Marra, Comp. Chem. Eng. 82 (2015) 273–282.