Advancement on heat transfer modelling of oxidation processes in Jet Stirred Flow Reactors

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Abstract
The paper investigates the role of the heat transfer in Jet-Stirred Flow Reactor (JSFR). Through the parametric continuation analysis of a lean and very diluted hydrogen/oxygen/diluent mixture in a non-adiabatic PSR and the experimental studies on JSFR, the paper demonstrates that some classical global heat transfer correlations for this class of system are not adequate to achieve quantitatively correct predictions.

Introduction
The current environmental challenges are driving the development of new combustion concepts. However, despite the progresses in the application of these concepts to practical systems, unresolved issues on the stabilization, auto-ignition, and structure of the reaction zone remain. Hence, large-scale implementation of advanced combustion processes is hampered by the risks associated with adopting relatively unknown new techniques. Indeed, combustion processes of hydrocarbons and related compounds can evolve with complex dynamic behaviors, originating from non-linear dependence of relevant variables [1]. Moreover, in open systems, by contrast to chemical reactions in closed vessels, multiple permanent/oscillatory stationary states can be achieved [2]. Conditions at which a transition from one state to another occurs in response to a continuous change in control parameters identify critical phenomena such as discontinuous jumps, or bifurcations [3], which are undesirable during combustion.
Therefore, it is important to establish these conditions and to understand both the factors that govern the stability of stationary states and those that give oscillations. In addition, since most chemical kinetic models have been validated at higher temperatures and low dilution, there is a need of optimal experiments to restrict uncertainties for low temperatures and high dilution conditions. These targets become fundamental because of the uncertainty of the kinetic models available in the literature to reproduce the oxidation behavior even of standard fuels in the presence of high dilution levels. Therefore, the ability to simulate each different dynamic behavior of reacting systems and its parametric range of existence can be used as an auxiliary, yet stringent, test of kinetic mechanisms [4].
A formidable tool for the observation of the dynamic variety is undoubtedly the Perfectly (also known as Well) Stirred Reactor (PSR). With such system, steady

states and sustained oscillations may both be preserved indefinitely. Jumps from one state to another and regions of multi-stability can be found [3].
PSR systems have been successfully applied to the oxidation of hydrocarbons and oxygenates [5]. However, most of these studies have been concerned with kinetic and mechanistic aspects only. But none of the overall phenomena under discussion arises solely from kinetics. Heat release and heat dissipation rates are integral to the development of events. In non-adiabatic conditions the heat loss brings about a decoupling of the fixed relationship between concentration and temperature. The two variables can change independently of each other and both must be specified to fully characterize the system. With this extra degree of freedom different patterns of behavior, including sustained oscillations, can result [1].
The main purpose of this paper is to investigate the importance of the heat loss in this simple thermo-kinetic system at low temperatures in lean and very diluted conditions. Particularly, the significance of the heat transfer coefficient model in the numerical analysis of the PSR is evaluated. To these ends both numerical and experimental study are carried out. The hydrogen is adopted as reference fuel in order to simplify the analysis by reducing the complexity of the kinetic aspects.

Experimental and numerical tools

The experiments were carried out in a spherical quartz Jet-Stirred Flow Reactor (JSFR) of 1.13e-4 m^3. Uniform temperatures and concentrations of reactants are achieved within the reactor by jet stirring. The reaction vessel and pre-heating assembly are located within two electrically heated recirculating-air ovens bounded by refractory walls. An electronic control of the ovens gives temperatures that are uniform to within ± 5 K over the vessel external surface and constant in time to within ± 0.5 K. The two ovens temperatures (then the reactor wall temperature) are monitored continuously by two Nicrosil-Nisil thermocouples.
Hydrogen, oxygen and diluent are each drawn separately from cylinders and filters that retain particulate impurities. Precise control of gaseous flow rates is achieved by means of thermal mass flow controllers upstream of the vessel. 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 in the vessel is measured continuously by means of a pressure transducer connected to the outlet from the vessel. For this series of experiments P was maintained at 111457.5 Pa.
The vessel is washed with nitrogen before use. Normally, an initial condition is set which represents the displacement of a non-reactive gas from the vessel by the reactants at the operating pressure and temperature. Once reactants flows have been established to match the required composition, total pressure and mean residence time in the vessel, the fuel is injected. Thermal equilibrium is established after any 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.

The temperature inside the reactor is monitored with a Pt/Pt-13% Rh thermocouple by employing a very fine junction (200 μm diameter wire), introduced near the center of the vessel through a horizontal entry arm. The thermocouple response is sufficiently rapid to give faithful record of all temperature changes occurring in the reacting gas. The combined response time for the sampling system and the acquisition is roughly 0.03 s.

When a steady state has been established, the response of the system to large or small, artificially induced, perturbations may be studied by temporarily changing the equivalence ratio (thus inducing a small temperature perturbation) or by momentarily stopping the flow of fuel (a large perturbation). The consequences reveal the nature of the steady state.

Reactants and molecular products compositions during the reaction were measured directly by gas chromatography. Samples for analytical measurements were sent continuously from the reaction vessel directly to a gas chromatograph valve via the exhaust tube without any pumping system. Rapid quenching of the reactant composition was achieved with a water-cooling system. A cold trap upstream of the valve removes readily condensable fractions that might otherwise block the jet.

Chemical analyses of the exhaust gas were undertaken principally to determine the extent of reaction, by monitoring the concentration of oxygen and hydrogen.

Mathematical models

The governing ordinary differential equations of the non-adiabatic, constant pressure PSR can be given as [6]:

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

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 coefficient depends on pressure, temperature, composition and flow rate. Since in JSFR the heat transfer coefficient depends on fluid dynamic conditions generated by gas streams outflowing from nozzles, it is impossible to vary residence time and heat transfer coefficient independently. Heat transfer for JSFR reactors has been firstly studied by David et al. [7]. They developed an empirical correlation for

cylindrical geometry based on Reynolds number evaluated on nozzle conditions (Re_N). Since operative conditions and reactor geometry of interest are different from those of David et al., the appropriate heat transfer correlation for spherical geometry developed by Lignola and Reverchon [8] is adopted in this work:

$$U = 0.89\mathrm{Re}_N{}^{0.683}\mathrm{Pr}^{1/3}\frac{k}{D} \tag{2}$$

where k is the thermal conductivity of the gas mixture, D is the reactor internal diameter and $\mathrm{Pr}=\mu c_p/k$ is the Prandtl number (μ is the dynamic viscosity). In this work, it was assumed that two of the contributions considered in [8], 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. [9]; the optimized kinetic model of H_2/CO combustion proposed by Davis et al. [10]; the detailed mechanism for hydrogen oxidation developed by Politecnico di Milano [11, 12]. Different mechanisms are taken into account in order to isolate the effects depending on heat transfer from those depending on kinetic phenomena.

Results

The effect of the feed mixture temperature (continuation parameter) on the bifurcation behavior of a lean hydrogen/oxygen/diluent mixture (equivalence ratio $\phi = 0.5$) in a non-adiabatic PSR is studied by using the parametric continuation tool introduced in [13, 14]. The hydrogen oxidation is analyzed in very diluted conditions; the mole fraction of the diluent is set to 0.94. Two different diluents are considered: nitrogen and a mixture nitrogen/water (60% N_2 – 40% O_2).

Since the global heat transfer coefficient depends on fluid dynamic conditions generated by gas streams outflowing from nozzles and thus on the diluent choice and on the continuation parameter, it is not assumed constant, but it is computed by the equation (2) at each equilibrium point.

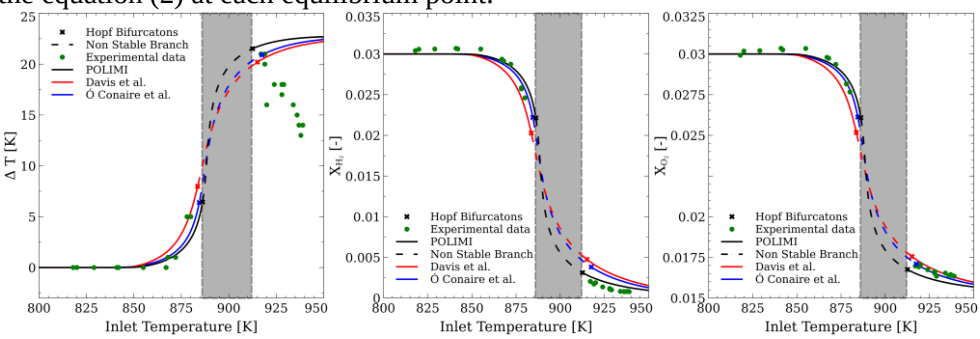

Figure 1. States in the JSFR as function of inlet temperature for the $H_2/O_2/N_2$ mixture. From left to right ΔT and mole fractions of hydrogen and oxygen.

The comparison between experimental data and the parametric continuation

analysis obtained with nitrogen as diluent are reported in Figure 1. The reported temperature increment in the reactor ΔT is defined as the difference between reactor temperature and the feeding mixture temperature.

Figure 1 shows that the predicted mole fractions of the reactants are in very good agreement with experimental data. Furthermore, the Hopf bifurcation points appear to be congruent with the region where an oscillatory behavior is experimentally detected (highlighted in gray in the figure). However, the temperature increment appears to be overestimated by the numerical model for feeding mixture temperature approximately greater than 915 K. Considering that these results are fairly independent from the choice of the reaction mechanism, this discrepancy may suggest that a correct evaluation of the heat transfer is important, and that the heat transfer correlation adopted is not adequate in modeling this system.

These results are partially confirmed by the comparison between experimental and numerical data obtained with nitrogen/water mixture as diluent (Fig.2).

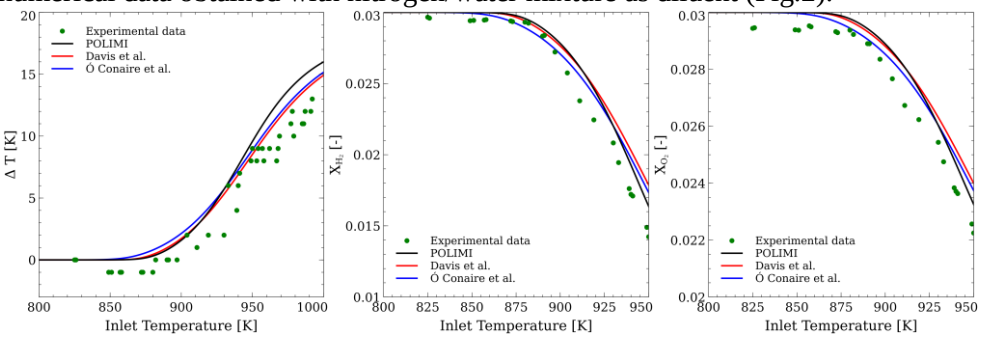

Figure 2. States in the JSFR as function of inlet temperature for the $H_2/O_2/N_2/H_2O$ mixture. From left to right ΔT and mole fractions of hydrogen and oxygen.

Indeed, also in this case the temperature of the reactor appears to be slightly overestimated by numerical analysis especially for the POLIMI mechanism. However, the differences reported in Fig.2 are not as significant as those obtained in the previous case due to the lower ΔT and then to the lower heat transfer rate.

Conclusions

The paper investigates the role of the heat transfer in the JSFR. The importance of this phenomenon is highlighted. Through the parametric continuation analysis of a lean hydrogen/oxygen/diluent mixture in a non-adiabatic PSR and the experimental studies on JSFR, the paper underlines not only that the heat losses must be included in mathematical models but also that classical global heat transfer correlation adopted for this class of system cannot be able to predict some phenomena. Particularly, the results show that there are significant discrepancies in the evaluation of the reactor temperatures when the nitrogen is adopted as diluent. Future works are needed in order to deepen this lack of understanding on heat transfer in JSFR. This aspect appears to be fundamental because JSFR are commonly used to validate reaction mechanisms.

References

[1] Griffiths, J.F., Scott, S.K., "Thermokinetic interactions: Fundamentals of spontaneous ignition and cool flames", *Prog. Energy Comb. Sci.* 13:161-197 (1987).

[2] Gray, P., Scott, S.K., "Archetypal Response Patterns for Open Chemical Systems with Two Components", *Philos. Trans. R. Soc. London, Ser. A* 332(1624): 69-87 (1990).

[3] Gray, P., Griffiths, J.F., Hasko, S.M., "Ignitions, Extinctions and Thermokinetic Oscillations Accompanying the Oxidation of Ethane in an Open System (Continuosly Stirred Tank Reactor)", *Proc. R. Soc. London, Ser. A* 396(1811): 227-255 (1984).

[4] Griffiths, J.F., "Reduced kinetic models and their application to practical combustion systems", *Prog. Energy Comb. Sci.* 21(1): 25-107 (1995).

[5] Simmie, J.M., "Detailed chemical kinetic models for the combustion of hydrocarbon fuels", *Prog. Energy Comb. Sci.* 29(6): 599-634 (2003).

[6] Glarborg, P., Miller, J.A., Kee, R.J., "Kinetic modeling and sensitivity analysis of nitrogen oxide formation in well-stirred reactors", *Comb. Flame* 65: 177-202 (1986).

[7] David, R., Houzelot, J.-L., Villermaux, J., "A novel and simple jet-stirred reactor for homogeneous and heterogeneous reactions with short residence times", *Chem. Eng. Sci.* 34(6): 867-876 (1979).

[8] Lignola, P.G., Reverchon, E., "A Jet Stirred Reactor for Combustion Studies: Design and Characterization", *Comb. Sci. Tech.* 60: 319-333 (1988).

[9] Ó Conaire, M., Curran, H.J., Simmie, J.M., Pitz, W.J., Westbrook, C.K., "A comprehensive modeling study of hydrogen oxidation", *Int. J. Chem. Kinet.* 36(11): 603-622 (2004).

[10] Davis, S.G., Joshi, A.V., Wang, H., Egolfopoulos, F., "An optimized kinetic model of H2/CO combustion", *Proc. Comb. Inst.* 30:1283-1292 (2005).

[11] Frassoldati, A., Faravelli, T., Ranzi, E., "Ignition, Combustion and Flame Structure of Carbon Monoxide/Hydrogen Mixtures. Note 1: Detailed Kinetic Modeling of Syngas Combustion also in Presence of Nitrogen Compounds", *Int. J. Hydrogen Energy*, 32: 3471-3485 (2007).

[12] Cuoci, A., Frassoldati, A., Buzzi Ferraris, G., Faravelli, T., Ranzi, E., "Ignition, Combustion and Flame Structure of Carbon Monoxide/Hydrogen Mixtures. Note 2: fluid Dynamics and Kinetics Aspects of Syngas Combustion", *Int. J. Hydrogen Energy*, 32: 3486-3500 (2007).

[13] Acampora, L., Mancusi, E., Marra, F.S., "Bifurcation analysis of perfectly stirred reactors with large reaction mechanisms", *Chem. Eng. Trans.* 43: 877-882 (2015).

[14] Acampora, L., Marra, F.S., "Numerical strategies for the bifurcation analysis of perfectly stirred reactors with detailed combustion mechanisms", *Comput. Chem. Eng.* 82: 273-282 (2015).