Numerical analysis of NOₓ production within a hydrogen catalytic combustor[#]

Francesco Battistella[1], Luca Mastropasqua[2], Alessandro Donazzi[1], Gianluca Valenti[1*]

1 Politecnico di Milano, Dipartimento di Energia. Via Lambruschini 4/a, 20156, Milano (Italy)

2 Hydrogen and Electrochemical Research for Decarbonization (HERD) Lab, University of Wisconsin-Madison, WI 53706, United States
(*Corresponding Author: gianluca.valenti@polimi.it)

ABSTRACT

Hydrogen combustion reactions produce nitrogen oxides as a byproduct. They can be reduced by exploiting the catalytic combustion of hydrogen in a monolith. However, some nitrogen oxides can still be produced in the gas-phase of the catalytic combustor. The present work numerically investigates the production of nitrogen oxides as a by-product of the combustion of a lean air-hydrogen mixture in a catalytic monolith with an equivalence ratio lower than 0.3. The analysis is carried out with a 2D dynamic numerical model implemented in MATLAB. The model solves mass and energy balances in a domain describing a single channel of the monolith. The model involves a detailed reaction mechanism for the gas-phase combustion, including the subsets that model the production of nitrogen oxides. As a result, the model indicates that the catalytic combustor does not produce nitrogen oxides with an inlet hydrogen fraction lower than 9%$_{vol}$. Furthermore, the maximum value of nitrogen oxide at the outlet of the channel is lower than 0.4 ppm, obtained with the highest hydrogen fraction simulated in this work (12%$_{vol}$ inlet hydrogen fraction).

Keywords: Hydrogen, catalytic combustion, nitrogen oxides, lean mixtures

1. INTRODUCTION

Hydrogen is a crucial energy carrier in the context of energy transition. It can be utilized to produce electrical energy in fuel cells, as a feedstock for chemical production, and for residential and industrial heating. In the latter case, its exploitation relies mostly on the combustion reaction. However, the high adiabatic combustion temperature of a stoichiometric air-hydrogen mixture leads to a high production of nitrogen oxides [1]. This phenomenon must be considered as both nitrogen oxide and nitrogen dioxide have a strong impact on the environment and human health [2]. Therefore, NOₓ mitigation strategies are adopted to reduce emissions, such as a limitation of the flue gas residence time in the high temperature region of the combustor or the combustion of lean mixtures to lower flame temperature [3]. However, the biggest limitations of such systems are stability at partial load and unburnt hydrogen with very lean mixtures.

A possible solution to burn in a stable manner air-hydrogen mixtures is a catalytic system. The use of such combustors to have thermal power with low nitrogen oxides at the stack has been considered in the past [4]. This technology could process flammable mixtures to produce thermal power to be exploited in dryers or in the food industry. This could enable the complete decarbonization of such processes with the avoidance of pollutants at the stack.

Catalytic combustion of flammable mixtures has been considered in literature, as a stabilizer for combustors in non-stoichiometric conditions [5]. However, catalytic combustion also avoids the production of nitrogen oxides over the catalytic wall [6]. Consequently, the only nitrogen oxides at the outlet of a catalytic combustor are produced in the gas-phase. As a result, the calculation of the production of nitrogen oxides in a catalytic combustor requires the evaluation of both the gas phase combustion and the solid phase one, as well as the transport mechanisms occurring inside a channel of the combustor. In this framework, the novelty of this work lies in the numerical quantification of the nitrogen oxides produced by a catalytic combustor processing a lean air-hydrogen mixture. This task is performed through a numerical model of the mechanisms occurring inside a channel of the combustor. The investigation aims at providing process

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engineers with an estimation of the pollutants produced by a catalytic combustor by varying the inlet hydrogen fraction and consequently the outlet temperature.

The present work numerically investigates the production of nitrogen oxides as a by-product of the combustion of a lean air-hydrogen mixture in a catalytic monolith with an equivalence ratio lower than 0.3. Consequently, a channel of the catalytic monolith is modelled in MATLAB considering the possibility to have combustion on the solid wall (heterogeneous) or in the gas-phase (homogeneous). Finally, the gas-phase combustion mechanism also includes the subset related to the production of nitrogen oxides.

2. NUMERICAL MODEL

The numerical model focuses on a single adiabatic channel of a catalytic monolith for hydrogen oxidation [7]. The discretization in space is performed by adopting cylindrical coordinates. The model solves mass balances in transient condition in the gas phase considering all the species present in the mixture, as reported in equation 1 for the i-th species. This equation includes the gas-phase reaction rate for the i-th species, which is modelled with a detailed mechanism based on the GRI mech 3.0 database [8]. The model solves the energy balance in transient condition as well, as reported in equation 2.

The catalytic wall of the channel is analyzed with dedicated mass and energy balances also accounting for the catalytic surface located at the outermost radius of the channel, as reported in equations 3 and 4. In these equations, the solid-phase reaction rate is evaluated with global kinetics, adopting the main kinetic parameters from a dedicated study on honeycomb monoliths for hydrogen combustion [9]. In particular, these parameters are related to a platinum catalyst. Such a catalyst is chosen to enable a stable ignition of the mixture at ambient temperature. Moreover, the choice of global kinetics for the catalytic wall is motivated by the operation of the catalytic monolith in a mass transport-controlled condition. Furthermore, the reaction rate on the solid wall also accounts for the mass transport limitations due to internal transport within the catalytic layer [7]. Finally, the gas phase and the solid phase are considered in thermal equilibrium.

Boundary conditions account for the adiabaticity of the channel, as well as for the symmetry of the distribution of the reactants and of the temperature profiles; these boundary conditions are described in a previous work [7]. The velocity is assumed to be axial only, and the flow regime is assumed to be laminar with a fully developed velocity profile at the channel inlet. The mass conservation is guaranteed by the calculation of the axial velocity profile as a solution of the continuity equation in each node of the domain, as described in equation 5. Furthermore, the inlet velocity profile is calculated as in equation 6, because of the assumption of fully developed velocity profile at channel inlet.

The catalytic wall reaction rate physical properties are calculated with values from the GRI mech 3.0 database, implemented as a MATLAB function.

$$\rho \frac{\partial \omega_i}{\partial t} = -\rho v \frac{\partial \omega_i}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r}\left(r \cdot J_{i,r}\right) + \frac{\partial J_{i,x}}{\partial x} + r_{i,gas} * MM_i \tag{1}$$

$$\frac{\partial T}{\partial t} = \frac{1}{\rho c_p}\left[-\rho v c_p \frac{\partial T}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r}\left(r \cdot k_g \frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial x}\left(k_g \frac{\partial T}{\partial x}\right) + \left(\sum r_{i,gas} * \Delta H_i\right)\right] \tag{2}$$

$$r_{i,solid} \nu_i M_i \xi - \rho D_i \frac{\partial \omega_i}{\partial r} a_v = 0 \tag{3}$$

$$\left.\frac{\partial T}{\partial t}\right|_{r=R} = \frac{1}{\rho_s c_{p,s}}\left[-k_g \frac{\partial T}{\partial r} a_v + k_w \frac{\partial^2 T}{\partial x^2}(1 - \varepsilon_{cat}) - \left(\sum r_{i,solid} * \Delta H_i\right)\xi\right] \tag{4}$$

$$\frac{\partial \rho v}{\partial x} = 0 \tag{5}$$

$$v_{inlet}(r) = 2 * \frac{Q_{channel}}{A_{channel}} * \left[1 - \left(\frac{r}{R}\right)^2\right] \tag{6}$$

2.1 NOx formation pathways in air-hydrogen combustion

Nitrogen oxides produced with air-hydrogen lean combustion are calculated with a detailed mechanism [8]. They can be produced with three pathways: the thermal pathway, the N_2O pathway, and the NNH pathway [10]. The thermal pathway is described with the Zeldovich mechanism. The rate of the reactions included in the mechanism is strongly dependent on temperature. [11]. The N_2O pathway is composed of 3 reactions, also including a third body. Consequently, it is promoted at high pressures and with lean combustion. Finally, the NNH pathway is not negligible in hydrogen flames at short residence times in the reactor [10].

2.2 Parameters for the simulations

The results presented in the following section are obtained simulating the combustion of air and hydrogen inside a channel of the catalytic monolith in the conditions reported in table 1. The properties of the channel are related to a cordierite monolith and are derived from a previous work [7]. Furthermore, the channel has an inert section at the inlet to improve numerical convergency without affecting the simulation of the production of nitrogen oxides. Finally, the model is solved in time with a built-in solver in MATLAB (ODE15s), after discretizing the spatial domain with finite differences in a grid with 450 nodes.
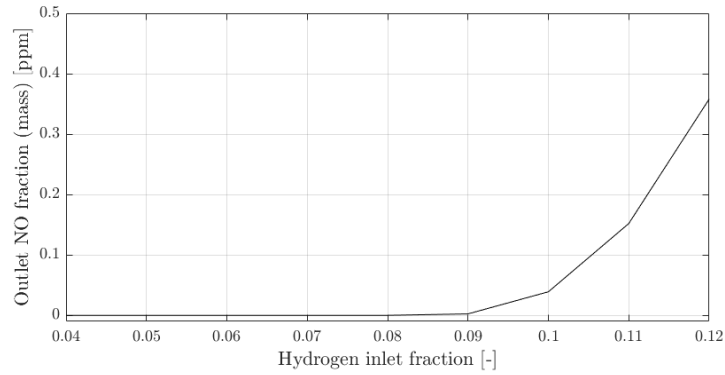
Figure 1 Nitrogen oxide at the outlet of the catalytic channel varying the hydrogen inlet molar fraction from

Table 1 Parameters used for the simulation of the operation of the channel of the catalytic monolith

Parameter	Value	Unit
Inlet hydrogen fraction (molar)	4%-12%	-
Inlet temperature	15	°C
Inlet velocity	7.3	m/s
Channel diameter	1	mm
Channel length	50	mm
Channel inert inlet section	5	mm
Solid wall thermal conductivity	2	W/(m K)
Solid wall density	2500	kg/m^3
Solid wall specific heat capacity	865	J/(kg K)

3. RESULTS

The numerical model gives indications about the fraction of reactants and products and about the temperature inside a channel of the monolith. The following figures report the results obtained in a steady state. This state is reached when all the time derivatives are zeroed.

Nitrogen oxide (NO) at the outlet of the channel of the catalytic monolith is reported in figure 1. Its fraction is lower than 0.4 ppm for all the air-hydrogen mixtures simulated. Furthermore, a hydrogen inlet fraction lower than 9% produces a negligible amount of nitrogen oxide. In all the cases simulated, nitrogen dioxide produced is lower than tolerance of the solver.

Another important parameter is the maximum temperature on the catalytic wall of the monolith [7]. This is related to a local disequilibrium in the limiting reactant and a Lewis number smaller than 1 [12]. As a result, the trend of maximum temperature reached at various hydrogen inlet fractions is reported in figure 2 together with adiabatic combustion temperatures.

Consequently, it is chosen to further evaluate the operation of the monolith with an outlet temperature lower than 850 K. This enables the operation with a temperature peak lower than 1250 K with the geometry
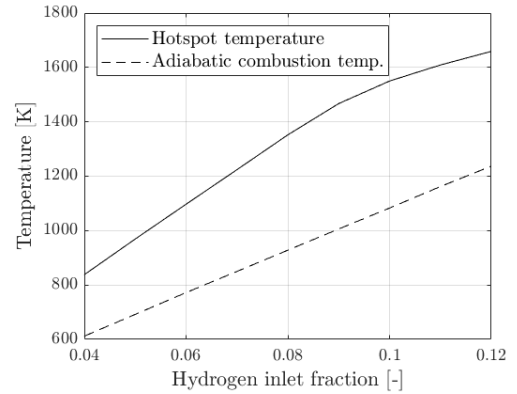

Figure 2. Hotspot temperatures over the catalytic wall and adiabatic combustion temperature varying the hydrogen inlet molar fraction from 4% to 11%.

simulated by the numerical model. This condition is achieved with a hydrogen inlet fraction equal to 7%. The following figures report the distribution of crucial parameters for the evaluation of the performances of the system. Figure 3 reports the field of hydrogen mass fraction inside the catalytic channel in this condition. As is noticeable, hydrogen is mostly consumed in the first millimeters after the inert inlet section. As a result, the fuel conversion is very high.

Figure 4 represents the distribution of hydroxyl radicals inside the catalytic channel. This species indicates the presence of gas-phase combustion, as it is included in the gas-phase reaction mechanism. The figure indicates that most of the gas phase combustion is occurring close to the catalytic wall, where the temperature is also located.

Figure 5 illustrates the temperature field inside the catalytic channel. The temperature peak is located in the first millimeters and is related to the Lewis number of the limiting reactant [5]. After the temperature peak, the temperature goes to the adiabatic combustion temperature for the air-hydrogen mixture considered in the simulation and reported in the previous paragraphs.
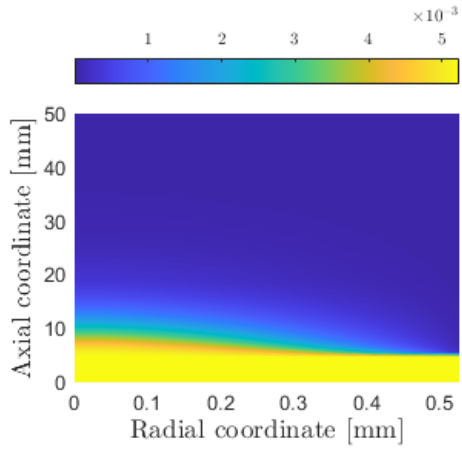
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Figure 3 Field of hydrogen mass fractions within the channel of the monolith in a chosen operational condition (hydrogen inlet molar fraction equal to 7%)
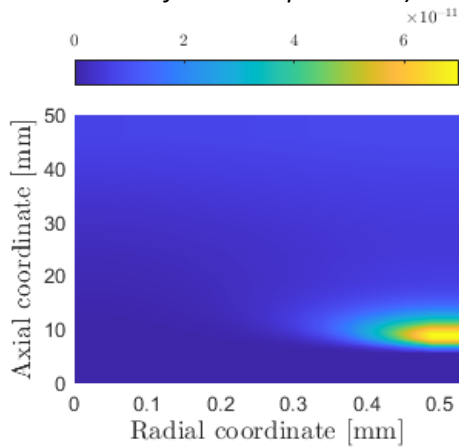

Figure 4 Field of OH radical mass fractions within the channel of the monolith in a chosen operational condition (hydrogen inlet molar fraction equal to 7%) to assess the position of the most active region in the gas phase.
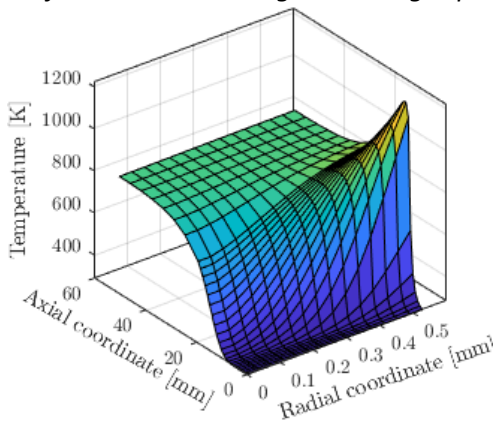

Figure 5 Field of temperature within the channel of the monolith in a chosen operational condition (hydrogen inlet molar fraction equal to 7%)

4. DISCUSSION

The nitrogen oxide fraction at the outlet of the catalytic combustor is very low in all the simulated conditions. As a result, it is possible to have a hot air flow (up to 850 K) in a stable manner and without the production of pollutants. Such a result is achieved thanks to the low temperature in the whole channel, as in the temperature hotspot temperatures are lower than 1250 K in the chosen operational condition. Furthermore, most of the fuel is converted in the solid phase where nitrogen oxides are not produced [6].

The temperature peaks over the catalytic wall are higher than the threshold that might initiate accelerated degradation mechanism. Consequently, the durability of the catalytic monolith must be evaluated, also considering the catalyst adopted for the oxidation of the air-hydrogen mixture.

The performance of this device is comparable with what can be achieved by flame combustors when considering outlet temperature. However, the operation at partial load is achieved without stability issues, as the catalytic combustion of a lower flow rate of reactants is not affecting the reaction rate over the solid phase as well as the diffusion mechanism towards the solid phase. Such a partial load operation is also simulated with the numerical model. Furthermore, the operation with lean or ultra-lean mixtures does not imply an incomplete fuel conversion, as might happen in a flame combustor. Finally, the production of nitrogen oxides is negligible in simulated conditions.

5. CONCLUSIONS

The present work numerically investigates the combustion of a flammable lean air-hydrogen mixture in a catalytic monolith with an equivalence ratio lower than 0.3. The novelty element is in the numerical quantification of the nitrogen oxides produced by a catalytic hydrogen combustor processing such a mixture. The task is accomplished by modelling the combustion inside a catalytic monolith considering both the gas-phase and the solid-phase reactions. Ultimately, the following results are obtained.

- A catalytic combustor produces a negligible amount of nitrogen oxides, lower than 0.4 ppm, in the operational conditions simulated. These conditions involve an inlet mixture with $12\%_{vol}$ hydrogen fraction and ambient temperature (288 K).
- The temperature peak inside the catalytic channel is lower than 1250 K with a hydrogen fraction equal to $7\%_{vol}$ to avoid excessive temperatures over the solid wall that might

result in a degradation of the catalytic monolith

- The chosen operational condition enables an outlet temperature of 850 K with complete fuel conversion and stable operation at partial load.

As a result, the hot flow rate produced by the process can be used in dryers or in the food industry for a complete elimination of the environmental impact of those processes. Furthermore, an experimental validation of the numerical model is currently being performed. In particular, the validation is focused on the verification of the production of nitrogen oxides downstream a cordierite monolith coated with platinum catalyst on an alumina washcoat. Finally, processing flammable mixtures enables the exploitation of other catalysts. Therefore, the test rig developed for the validation of the numerical model is also being exploited for such an investigation. The results will be included in future work.

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