METHANE COMBUSTION IN A CATALYTIC MONOLITH AT ELEVATED PRESSURES


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Abstract
The effect of pressure on catalytic combustion of methane in a perovskyte-based monolith is here investigated both experimentally and numerically. Results show that only the coupling between catalytic and homogeneous reactions allows achieving a complete methane conversion. As the operating pressure increases, the catalytic reaction is activated, thus behaving as a pilot for sustaining the homogeneous reaction which allows overcoming the mass transport limitations at the catalytic surface.

Introduction
In view of its ability to burn different fuels beyond their flammability limits with high efficiency even at relatively low temperatures, thus producing extremely low levels of pollutants (NOx, CO and UHC), catalytic combustion (CC) is a promising technique for high-efficiency clean combustion [1]. Despite of this strong interest, its wide diffusion in power and heat production systems has been limited because of several issues related to the high cost of catalysts, generally based on noble metals, and to the low thermal resistance of materials [1]. Due to such limitations, complex process designs including additional homogeneous stages have been proposed [2]. Nevertheless, the combustor design, even for hybrid combustion, is strongly dependent on the catalyst performances in terms of both activity and thermal stability [2]. The use of noble metal catalysts, most notably Pd, limits the temperature in the catalytic stage well below 1000 °C, because of the metal tendency to volatilize and/or sinter and/or change oxidation state into a less active one at temperatures around 700 °C [1,2]. As a consequence, the use of active phases resistant to temperatures of 1000 °C could enable a more efficient combustion in the homogeneous zone, resulting in an overall performance improvement and/or compactness of the post catalytic stage. Perovskites meet the above mentioned requirements and are also less expensive than noble metals. These mixed oxides have been extensively considered as total oxidation catalysts [3,4]. Nevertheless, the application of perovskites is limited by their low surface area. In order to overcome this problem, different research groups have dispersed active phases on high surface area supports (La-stabilized alumina or MgO) with an increase of activity and thermal stability [3].
Even if generally related to GT applications, most of the papers devoted to CC report experiments performed at atmospheric pressure, while few studies have been conducted at higher pressures and only on noble metal catalysts [5]. This lack of knowledge is more remarkable if the complexity of a catalytic process is considered especially noting that catalytic systems often turn out to be more active in lab-scale test rig than at higher pressure [6]. In this work, self-sustained methane combustion over a 20 % wt LaMnO$_3$/La-γAl$_2$O$_3$ monolith was experimentally studied under conditions relevant for small size GT applications (temperature up to 800°C and pressure up to 11 bar) in a lab-scale homemade test rig.

The work focuses on the bifurcational behavior of the catalytic combustor, in particular the ignition phenomenon. Experiments have been used to validate a CFD model with a simple reaction rate [5]. After validation, the hetero-homogeneous pathway interplay was analyzed in order to elucidate the main features of the behavior of a catalytic combustor for different operating pressures. Simulations have been carried out in order to elucidate the effects of heat losses and the support thermal conductivity.

**Experimental**

Lean methane combustion under self-sustained conditions was performed over a 20 wt% LaMnO$_3$/La-γ-Al$_2$O$_3$ catalyst supported on 900 cpsi honeycomb cordierite monolith (NGK) in a shape of cylinder (length, 50 mm; diameter, 11 mm). The catalytic monolith was prepared according to a procedure reported in [4]. About 1.4 g of catalyst were deposited onto the substrate.

The monolith was placed between two mullite foams (thermal shields) and wrapped in a ceramic wool tape before being inserted in a cylindrical stainless steel reactor. An heating jacket (Tyco Thermal Controls) provided for the reactor pre-heating. Two thermocouples were placed inside the reactor at the centre of the first thermal shield (or pre-heater) ($T_{pre}$) and at the centre of the monolith ($T_{cat}$). Moreover, a third thermocouple ($T_w$) was placed close to the external steel wall and the heating jacket.

The tests were conducted in a lab-scale home-made set-up designed to work up to 12 bar and were conducted at fixed pre-heating conditions and varying the pressure from approximately 1 bar up to 10-11 bar. The mass flow rate was kept constant.

**Model**

A two-dimensional CFD model was developed to simulate the coupling of the fluid flow and the chemical processes at the gas-solid interface and in the gas phase for lean methane/air combustion. The central channel of the monolith reactor was simulated, which is the more adiabatic one, therefore, all channel walls were considered adiabatic. The reaction rate for homogenous methane combustion was calculated according to the single-step reaction rate by Westbrook and Dryer [7]. The catalytic reaction rate used in the present work was obtained from an
independent experimental campaign on the LaMnO$_3$/La-γ-Al$_2$O$_3$ catalyst performed in the pressure range 1-12 bar and is reported in [5]. The model equations were discretised using a finite volume formulation on a structured mesh built by means of the Gambit. Computations were performed by means of the segregated solver of the ANSYS FLUENT code (release 13) that adopts the SIMPLE method to treat the pressure-velocity coupling.

**Experimental results and model validation**

In Fig. 1, the CH$_4$ conversion and temperatures are plotted as a function of the pressure. It is observed that methane conversion increases by increasing pressure. This is due to the longer contact time and faster reaction rates. Two main branches can be identified: at pressure lower than 5 bar, the methane conversion increases up to about 40%; at pressure higher than 5 bar, a change of slope is found and complete methane conversion is attained, suggesting that between 4 and 5 bar ignition occurs. The $T_w$ and $T_{pre}$ exhibit the same trend of the methane conversion. On the contrary, $T_{cat}$ increases up to 5 bar and then starts decreasing due to shifting of the reaction front upstream [4]. The experimental and simulation results for CH$_4$ combustion at 88 slph are shown in Fig. 2 in terms of methane conversion as a function of the pressure. The full symbols (open symbols) represent experiments and simulations performed increasing (decreasing) the operating pressure.

![Figure 1](image_url)

**Figure 1.** Conversion and temperatures as a function of the operating pressure; total flow rate = 31 dm$^3$/h (STP); O$_2$ = 10%; CH$_4$ = 3.7%; N$_2$ = balance.
Figure 2. Comparison of experimental (●, ○) and predicted (▲, △) conversion as a function of the operating pressure. Experiments and simulations performed by increasing P (full symbols) and decreasing P (open symbols). $Q_{\text{tot}} = 88 \text{ dm}^3/\text{h}$ (STP); $O_2 = 10\%$; $CH_4 = 3.7\%$; $N_2 = \text{balance}$.

Also in this figure, it is possible to identify two different branches: the first branch at lower pressure and the second one at higher pressure. The pressure value at which the passage from the first branch to the second branch (i.e. ignition) occurs is about 7.5 bar in the experiments and 8 bar in the simulations. At lower flow rate (see Fig. 1), the passage occurs at lower pressure ($P = 5$ bar). This effect can be attributed to the increased contact time obtained at low flow rate. The model underpredicts the methane conversion on the lower branch, but catches the passage from the first to the second branch. It is worth noting that, in both experiments and simulations, a steady state multiplicity is found.

In Fig. 3, the maps of temperature ($T$), $CH_4$ molar fraction and homogeneous reaction ($R_v$) are shown as obtained at 9 bar. It is found that, after few millimeters from the channel entrance, the homogeneous reaction starts at the wall ($R_v$). The fronts of methane molar fraction and temperature well reproduce the front of the homogeneous reaction, suggesting that the increase in methane conversion and temperature mainly occurs through the front of the homogeneous reaction.

In order to weight the role of the homogeneous reaction with respect to the catalytic reaction, we performed simulations by artificially neglecting or the homogeneous either the heterogeneous reaction. We found that in the absence of the catalytic reaction, in the range of the operating pressure investigated (1 - 12 bar), the methane conversion is negligible.
In Fig. 4, the methane conversion is plotted as a function of the operating pressure as obtained by including (▲) and neglecting (●) the homogeneous reaction. In the absence of the homogeneous reaction, the passage from the lower branch to the upper branch occurs at the same pressure value of the full model (P = 8 bar), suggesting that ignition depends exclusively on the catalytic reaction. However, it is worth noting that, in the absence of the homogeneous reaction, even at pressure higher than 8 bar, the methane conversion is incomplete indicating that, under these conditions, the surface reaction is controlled by the methane transport toward the catalytic surface.

Simulations have been carried out in order to elucidate the effects of heat losses and support thermal conductivity. Results (not reported) show high sensitivity of the reactor performances to these parameters. In particular, in both cases methane conversion significantly decreases due to the reduction of the mean temperature of the catalyst.

Conclusions
Experiments performed in a monolithic reactor at high pressure show that the reactor performances are strongly sensitive to the operating pressure. Ignition pressure is a function of operating conditions, such as flow rate and fuel concentration.

Steady state multiplicity and then hysteresis behavior have been found when assuming the operating pressure as the bifurcation parameter. The model results show that the complete methane conversion is attained by the synergic coupling between catalytic and homogeneous reactions. The catalytic reaction has been proven to promote ignition and high wall temperatures. Such conditions allow initiating and sustaining the homogeneous reaction front which completes the methane conversion.
Figure 4. Methane conversion as a function of the operating pressure as obtained by the full model (▲) and by artificially neglecting the homogeneous reaction (●).

\[ Q_{\text{tot}} = 88 \text{ dm}^3/\text{h (STP)}; \text{O}_2 = 10\%; \text{CH}_4 = 3.7\%; \text{N}_2 = \text{balance} \]

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References

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