Mild Combustion of Pure Hydrogen and Hydrogen-Based Fuels

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1. Introduction

The reduction of pollutant emissions from practical combustion devices is a major issue in combustion researches. One of the main pollutants is NOx and several technologies have been proposed, in particular, to reduce NOx emissions production. These methods usually try to reduce the residence time of gases in high temperature regions of the burner, or to avoid high oxygen concentration in these regions. In the last few years, significant efforts have been made to obtain high thermal efficiencies, due to air-preheating, without the adverse effect of high NOx emissions caused by flames at high temperatures [1-3]. It was found that a strong exhaust gas recirculation combined with air preheating generates relatively low flame temperatures. The combustion air is diluted with a large amount of recirculated gases, so the concentration of oxygen within the reaction zone is much lower than in the case of undiluted air allowing for a better control of the furnace temperature. This combustion technology is commonly defined as flameless [4-5] or mild combustion [6]. Despite design guidelines and operating conditions to sustain flameless oxidation are available for standard fuels, namely methane or natural gas [3, 7-8], much less information are available for other fuels. The purpose of this work has been to investigate and define, experimentally, operating conditions necessary to sustain flameless combustion of different non-conventional fuels. Precisely, a hybrid hydrocarbon-hydrogen mixture, CH4/H2 70/30% by vol., and pure hydrogen have been used as fuels. Pollutants emissions, mainly CO and NOx, have been monitored; these data have been reported in a diagram as a function of two main design parameters, the average furnace temperature and the dilution ratio, respectively, to define the operating flameless conditions for the investigated fuels.

It has been demonstrated that, in flameless conditions, hydrogen high reactivity allows working with particularly low temperatures and high dilution factors with respect to other fuels behavior.

2. Experimental section

To achieve flameless conditions, high internal turbulence and premixing of combustion air with exhaust gases are required within the combustion chamber; for this reason a burner provided by a single high-velocity jet nozzle has been used. As the laboratory-scale equipment has been described in details elsewhere [7-8], the burner has been sketched in figure 1 and its main characteristics are briefly summarized in the following. The experimental apparatus is constituted by the burner, a flow rate control section for the reactants feeding, and a sampling and measurement section for the detection of temperatures and exhaust gases compositions. The laboratory-scale burner is a quartz tube divided in two main parts: the combustion air preheating zone (lower part, filled by quartz pellets to enhance heat exchange, D), and the combustion chamber (upper part). With reference to figure 1, fuel and air enter the combustion chamber through a single high-velocity nozzle. This nozzle, located on the bottom of the combustion chamber, constitutes the burner core, into which fuel is fed perpendicularly through a capillar pipe (A); it is also possible to notice the positions of other reactants inlets, namely port B for the incoming flow rates of primary air and inert gas and port C for the secondary air flow rate, thermocouples and the sampling point of the
gas analyzer. Gas sampling has been performed by an on-line gas analyzer (HORIBA PG–250), which allows for measuring the concentrations of nitrogen oxides, oxygen, carbon monoxide and carbon dioxide. Moreover, three thermocouples have been located at different heights into the furnace to monitor the thermal field inside the combustion chamber.

![Schematic diagram of the experimental-scale burner used for the experiments.](image1)

**Fig. 1** Schematic diagram of the experimental-scale burner used for the experiments.

It is a widespread opinion [4, 9] that the dilution ratio inside the combustion chamber, $K_V$, plays a key-role determining flameless burner working conditions. As a consequence of several calculations performed with a general–purpose code for computational fluid dynamics [7] and accounting also for both internal and external recycle as well as the presence of a secondary air inlet, which flow rate is lower than the entrained one, the $K_V$ can be computed as:

$$K_V = \frac{R - S / A}{1 + S / A} + \frac{(I / A) \cdot (R + 1)}{(1 + F / A) \cdot (1 + S / A)}$$  \hspace{1cm} (1)

where A and S are primary and secondary air, respectively, I is the inert gas flow rate, F the fuel flow rate and R the maximum value of the recycle factor imposed by the jet presence in the chamber; its value is equal to about 5 for all the conditions investigated.

A usual representation of the influence of $K_V$ on the combustion characteristics involves $T$ vs. $K_V$ diagrams as shown, for the sake of example, in figure 2.

![T vs. Kv diagram sketching boundaries and peculiar regions identified in this work.](image2)

**Fig. 2** $T$ vs. $K_V$ diagram sketching boundaries and peculiar regions identified in this work.
This diagram reports five main areas: clean flameless combustion region (B), where flameless conditions can be easily maintained without any significant pollutant emission; mixed zone (A), where both low-emissions and flameless conditions can be achieved depending on the experimental conditions, such as a selection of a suitable combustion air preheating temperature; thermal NOx region, where flameless conditions can be sustained but thermal NOx production becomes significant; no combustion (or extinction) zone and traditional flame combustion region.

Since it is not possible to directly operate the burner in a flameless mode, it is necessary to follow an experimental procedure to achieve flameless conditions; for this reason, the burner is initially conducted in flame-mode to heat-up the combustion chamber until high temperatures are reached within the furnace, then a transition towards flameless or mild conditions is operated, essentially increasing the dilution ratio. This procedure involves four main steps:

1. Ignition and furnace preheating; reactants entering the burner are electrically ignited. A small amount of air is fed through the nozzle while a secondary air stream is flushed around the nozzle to stabilize a diffusion flame over the tip, allowing for the combustion chamber preheating;

2. Transition from traditional combustion to flameless conditions; this is achieved by gradually decreasing the secondary air flow rate and increasing the primary combustion air flow rate through the nozzle, generating a high velocity jet that increases the dilution ratio value until, behind a given value of $K_v$, the system enters in the flameless region: this $K_v$ value defines the vertical boundary of the flameless region.

3. Cooling; the lower horizontal boundary of the flameless region is defined reducing, at a constant $K_v$, the preheating furnace temperature so as to cool the combustion chamber. As a consequence, the velocity of the fuel oxidation reaction partly decreases and the formation of carbon monoxide begins. The fuel conversion to CO$_2$ and water reduces progressively as a function of the “forced” decrease of the furnace temperature, leading the system out of mild combustion boundaries, towards no combustion conditions;

4. Heating; the upper horizontal boundary of the flameless region is defined increasing the preheating furnace temperature after the system has reached stable mild conditions. The average furnace temperature rises until a thermal-NOx formation threshold is reached; above that temperature limit, the NOx formation increases.

Concerning the experimental procedure, the burner has been ignited and conducted from the beginning with a selected composition of the CH$_4$/H$_2$ mixture used as fuel; on the other hand, tests regarding the use of pure hydrogen as fuel, mainly for safety reasons, have been carried out according to a slightly modified experimental procedure: the burner has been ignited and stable mild combustion conditions have been achieved with a hybrid CH$_4$/H$_2$ 40/60 by vol. fuel mixture, then the hydrogen content within the fuel is progressively increased until a pure hydrogen flow rate is fed to the burner. Once stable conditions, in terms of temperature and pollutants concentrations, are obtained with pure hydrogen, the previously described experimental procedure is followed to identify mild combustion boundaries.

3. Results and discussion

Flameless conditions can be practically identified by both the flame disappearing and the reduction of temperature gradients inside the furnace; this usually means a sudden reduction of NOx emissions but CO$_2$ yield still higher than 50%. Since the goal of flameless combustion is lowering pollutants emissions, a clean flameless condition has been also defined, adding to the previous criterion an additional requirement concerning a maximum pollutants concentration within the exhausts, as summarized in table 1:
First of all, a non-conventional hybrid fuel with composition CH₄/H₂ 70/30% by vol. has been used. The operating map obtained experimentally has been reported in figure 3; in particular, empty symbols have been used to represent non-clean combustion conditions while full symbols describes clean flameless conditions, according to table 1 limits. It is possible to identify, on the operating map, two different main regions: a “mixed” zone (marked by letter A) and a clean flameless region (B). For the investigated hybrid fuel, it can be also notice that the clean flameless combustion region is enclosed by three limits. An upper horizontal one, strongly influenced by the furnace temperature which could activate and/or control radicals reactions responsible for the formation of thermal-NOₓ (Zeldovich mechanism). The lower temperature threshold that could be easily identified gradually cooling the combustion chamber; below the threshold temperature the combustion efficiency decreases leading to an excessive formation of CO, with a subsequent reduction of the CO₂ yield. Finally, the lower Kᵥ threshold defines the minimum value of the recycle ratio necessary to ensure a strong dilution of internal gases that could allow the disappearance of the front flame and the achievement of stable clean mild combustion conditions. Within the “mixed” zone, it is theoretically possible to sustain a clean combustion, but not always the system achieves clean conditions. This could be ascribed mainly to the hydrogen high reactivity, that confers a high stability to the flame anchored on the nozzle reducing the possibilities to obtain the disappearance of the flame front and a transition from traditional to mild conditions.

![Flameless operating map for a hybrid 70/30% CH₄/H₂ fuel mixture @ 3% O₂ excess.](image-url)

In the higher temperature region, the transition towards clean flameless evidenced by hydrogen-containing fuels leads to “hot–spots” inside the furnace with temperature values
higher than the average furnace temperature; sometimes, it is possible to find NO\textsubscript{x} emissions higher than those expected according to the detected temperatures. In particular, this behavior is evidenced during tests carried out with a strong preheating (namely above 900°C) of the combustion air, thus leading to a bended boundary in the upper part of the mixed zone. The hydrogen presence within the fuel, as its maximum laminar burning velocity in air is more than 6 times higher than the corresponding one of methane, did not allow to operate the burner with a relatively low-velocity jet at the nozzle tip; for this reason, as clearly found for an hybrid 70/30\% CH\textsubscript{4}/H\textsubscript{2} fuel at a fixed value of Kv = 5 (figure 4), it is necessary to increase the jet velocity above a critical value (equal to about 75 m/s for these fuels) to obtain a marked decrease of NO\textsubscript{x} emissions and the possibility to attain clean flameless conditions also with hybrid CH\textsubscript{4}/H\textsubscript{2} mixtures.

![Graph](image)

*Fig. 4 NO\textsubscript{x} concentration as a function of jet velocity at constant Kv = 5 for the CH\textsubscript{4}/H\textsubscript{2} 70/30\% fuel.*

Hydrogen represented the last fuel investigated in this study. The operating map has been reported in figure 5. As observed with hybrid hydrogen-hydrocarbons mixtures, it is clear that hydrogen is able to sustain a clean flameless combustion also in conditions where pure methane combustion produces large amount of CO; this is related to the more reactive characteristics of the hydrogen that is able to create a large pool of radicals that lead the hydrocarbon oxidation to be complete. Therefore, it is clear that operating the burner with pure hydrogen it is possible to define a clean combustion zone larger than that obtained with the hybrid mixture: at a dilution ratio of about 5 and for temperatures lower than 490°C it is still possible to sustain a mild combustion of pure hydrogen.

As previously mentioned, the slightly different procedure adopted to identify mild combustion stability limits when the burner is operated with pure hydrogen allow for identifying an operating map which reports only the flameless clean region (figure 5); in particular, the absence of carbon–containing species within the fuel removes the possibility to clearly identify a lower temperature threshold, which usually is individuated by a worsening of the combustion process and a large CO depletion. However, it is possible to identify an upper temperature boundary at a temperature of 990°C, that is quite close to the limit detected for the hybrid CH\textsubscript{4}/H\textsubscript{2} 70/30\% fuel (T=1050°C), thus indicating that this threshold is quite insensitive to the kind of fuel.
4. Conclusions

In this study, experimental tests allowed for demonstrating the feasibility of mild combustion both for hybrid fuels constituted by a methane/hydrogen mixture and for pure hydrogen as fuel. The obtained results showed how, for a hybrid mixture CH₄/H₂ 70/30% by vol., it is possible to achieve clean combustion modality at a temperature of about 850°C inside the combustion chamber and a minimum dilution ratio of about 5. However, using pure hydrogen as fuel, the clean zone boundaries are increased allowing to sustain a stable mild combustion at temperatures resolutely lower than ones obtained for hybrid methane/hydrogen mixtures.

5. References