Experimental investigation of stabilization and emission characteristics of ammonia/air combustion in MILD Combustion

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Introduction

In the context of world energy demand there is a broad agreement that effective and affordable methods for energy storage will be crucial in overcoming the inherent intermittency of renewable resources and increasing their share of generation capacity [1]. Among these methods, chemicals-based storage technologies offer the advantage of being able to store large amounts of energy for long periods of time. A prominent role among those energy carriers is quite often foreseen for use of hydrogen as an energy vector. However, issues associated with storage and distribution are still barriers to its wide diffusion [2].
On the other hand, following industrial interests, ammonia has been recognized as a hydrogen carrier fuel [3] and it burns without carbon oxides emissions, being a carbon-free molecule, thus it offers great potentialities to mitigate greenhouse gas emission [4].
A recent review article by Valera-Medina et al. [5] showed that ammonia could provide for a practical next generation system for energy transportation, storage and use for power generation, in virtue of its established transportation network and high flexibility. However, earlier applications and studies of ammonia as a fuel reported challenges and drawbacks associated with ammonia combustion [6, 7]. Recently, some works made at Tohoku University demonstrated that as the mixture equivalence ratio for different methane-ammonia blends increases towards stoichiometry, unburnt species such as NH_3, CO decrease in contrast to NO_x. A two-stage combustion system has been designed and tested to overcome such drawbacks[8].
Valera-Medina et al. [9] presented a series of studies burning mixture of ammonia and hydrogen/methane at different concentrations in as swirl burner. Results showed the complexity of stabilizing premixed ammonia blends. NOx and CO were considerably lower at high equivalence ratios > 1.10. Unfortunately the degree of knowledge is not yet sufficient to give a definitive explanation to the observed behaviors.
According to the general picture, features and potential advantages/drawbacks of using ammonia as fuel in advanced combustion technologies for stationary power generation, such as MILD [10], are also largely unknown. As matter of facts, to the best of the authors' knowledge, there are no studies in the literature that has shown the feasibility of MILD Combustion when pure ammonia is used as fuel.
Hence, the aim of this paper is to provide an insight into these practical issues, utilizing a cyclonic flow burner operated in MILD Combustion conditions, investigating ammonia-firing conditions.
The influence of operative parameters (preheating temperature, equivalence ratio and thermal power) on the system performance is also explored for stationary applications. Thus, this paper helps to bridge the gap between research, development and implementation for an innovative technology which has the potential to provide a sustainable energy system.

Experimental setup

The experimental campaign was carried out in the Laboratory Unit CYclonic (LUCY) burner reported previous publications of this research group [11, 12]. It consists of an alumina prismatic

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chamber (20x20x5 cm^3) externally covered with a heat-insulating material. It is located inside an AISI 310s stainless flanged case that can be easily opened for inspection operations. Several shielded thermocouples (type N) are used to monitor the combustion process. The flow injection configurations and the position of the exit (in the center of the bottom face of the chamber) induce a toroidal flow-field. The oxidizer flows are preheated by means of two heat exchangers to the desired inlet temperature (T_{in}) before entering the reactor. Fuel is fed into the combustion chamber at environmental temperature. The burner is located within electrical ceramic fiber heaters to minimize heat exchange towards the surroundings. The mixture inlet equivalence ratio can be easily changed (from ultra-lean to very rich conditions). The exhaust gases are sampled from the central outlet by a cooled probe and are analyzed through a portable Agilent micro-GC analyzer that allows to measure O_2, H_2, N_2. NO and NO_2 are measured by means of both a flue gas analyzer (TESTO 350) and a dedicated ABB analyzer. NOx concentrations are normalized to 15% O_2.

Results

The experimental campaign was carried out by operating LUCY burner with ammonia/air mixtures at atmospheric pressure. The performance of the cyclonic burner has been characterized in terms of system working temperatures (T) and pollutant emissions (NO_x) for several equivalence ratio (Φ) values of the mixture, in accordance with previous works [11]. Both the inlet preheating temperature and thermal power were changed. Experimental tests were realized for three values of the inlet preheating level (300 K, 600 and 900 K) and for a fixed value of the nominal thermal power P=5 kW, as a reference value for efficient working conditions identified in previous works with several hydrocarbon fuels [12, 13]. Figure 1 shows the mean system working temperature (T) and the characteristic residence times of the mixture (τ) by varying the equivalence ratio. As it is possible to note, the sustainability of the combustion process is ensured at 5 kW when the working temperature is higher than about 1250 K in the whole range of inlet preheating temperature and equivalence ratio here investigated. Working temperatures lower than 1300 K (dashed lines) should be avoided because of the occurrence of extinction phenomena. The dash lines and the grey area identify feeding conditions where global extinction behaviors were observed. Such extinction behavior was recognized in the same burner in previous works of the same group for methane and propane mixtures [14] suggesting that the oxidation process remains stable when the temperature inside the reactor is above 1050 K.
Noticeably, such threshold is higher in the case of ammonia-air combustion and therefore it could be stated that this behavior is related to the switch on high temperature kinetic branching of ammonia chemistry.

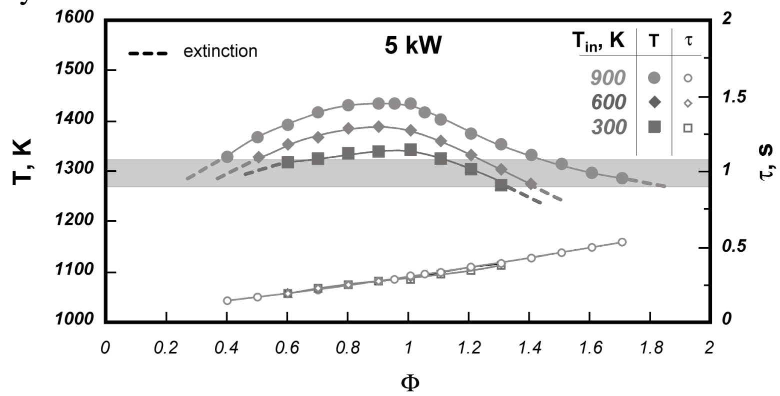

Fig. 1 Working temperature (T) and characteristic residence time (τ) for ammonia-air mixtures as a function of Φ for several Tin values at P = 5 kW.

Thus, Figure 1 shows that the range of stable operating conditions in terms of equivalence ratio is widened by increasing the preheating level of the inlet air-flow. In particular, at environmental

conditions (T_{in} = 300 K) a stable oxidation process has been obtained in the range 0.6 < Φ < 1.3, whereas by preheating the inlet oxidizer flow up to T_{in} = 900 K the system allows to achieve stable conditions in a wider Φ interval (0.4 < Φ < 1.7).
Figure 2 reports NO_x emissions at the exhaust for the same condition (P = 5 kW) by varying the equivalence ratio of the mixture, parametrically in the inlet preheating temperature. It shows that the minimum NOx emission levels are obtained when the burner is operated with stoichiometric/rich mixture compositions. In particular NOx emissions under lean conditions for Φ = 0.6, ranged from 250 ppm without preheating the oxidizers, to 1000 ppm for T_{in} = 900 K.
It is possible to observe that NOx emissions significantly decrease moving toward fuel rich conditions for all cases here investigated. Figure 2 shows that lean ammonia-air flames emit high levels of NOx and this result is slightly dependent on the preheating level. Thus, the stoichiometry is seen to have a major impact on the NOx formation [15]. Such results are in accordance with several literature works for ammonia-air combustion in model reactors or gas-turbine combustors [16]. The results reported in Figure 2 show that high values of the inlet preheating temperature of the air flow allows to lowering NOx emissions at 3 ppm when the system is operated with rich mixtures, while the opposite effect is obtained if the burner works under lean conditions (Φ<0.9), obtaining NO_x levels of about 1000 ppm. This suggests that the best performance in terms of NO_x emissions can be obtained in the operational window from stoichiometric to slightly-rich conditions (1<Φ<1.2).

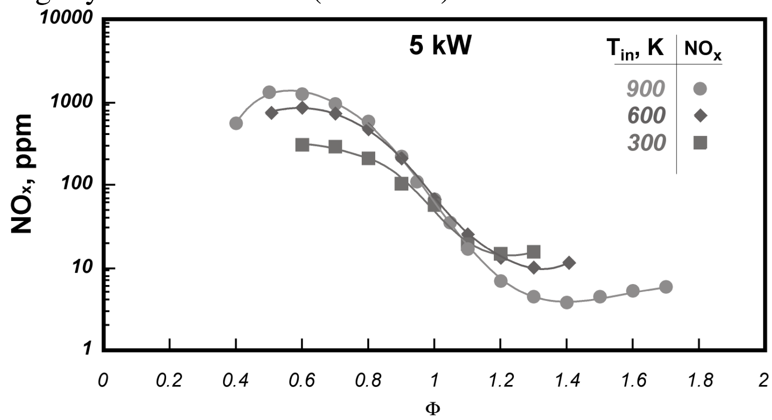

Fig. 2 NO_x emissions for ammonia-air mixtures as a function of Φ for several T_{in} values at P = 5 kW.

Conclusions

The main operational characteristics of ammonia/air combustion in a cyclonic burner were investigated through temperature and exhaust gas emission measurements. Results of the influence of main external operating parameters, such as equivalence ratio and inlet preheating level on system performance were presented. The appearance of flameless combustion conditions and the temperature values were used to investigate the stability characteristics.
In particular, MILD Combustion regime was achieved for a wide range of external parameters with reduced combustion peak temperatures and very low NOx emissions in a wide operational window. Remarkable performance in terms of stabilization of the oxidation process and low pollutants has been verified in a wide range of operating conditions.
The sustainability of the combustion process with ammonia is ensured when the working temperature is higher than about 1250 K for each condition investigated in this manuscript. Working temperatures lower than 1300 K should be avoided because of the occurrence of extinction phenomena with high emissions of unburned products.
In particular, the present work permits to identify a narrow reactor extinction range (1250 < T < 1350 K) also recognized in previous works for hydrocarbons combustion. The threshold is higher in the case of ammonia-air combustion since it is related to the switch on high temperature kinetic branching of ammonia chemistry.

The critical equivalence ratio above which there is a steep decrease in NOx emissions was found to be slightly above the stoichiometric value ($\Phi = 1.1$) for each condition here investigated. In this sense the best operational window in order to minimize NOx emissions seems to be in slightly fuel-rich conditions ($1< \Phi<1.2$).
The preheating the inlet air-flow allows to reach very low NOx emissions also for stoichiometric mixtures, while for lean mixtures lower emissions have been obtained without external preheating.

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