

HIGHLIGHTS

- The cyclonic burner permits to operate with ammonia in MILD Combustion
- Low NO_x emissions for stoichiometric and fuel-rich conditions were obtained.
- Stabilization of pure ammonia combustion was obtained in MILD Combustion conditions
- A unique extinction temperature range of the burner was identified for ammonia/air

1 **Ammonia MILD Combustion in a Cyclonic Burner**

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26 **Abstract**

27 Chemical storage in suitable energy carriers is a requirements of any
28 renewable sources based energy supply systems. Among the others
29 ammonia seems to be a very promising carrier due to its very high hydrogen
30 density and long established production processes. In addition, ammonia can
31 be directly used as a fuel for combustion systems without requiring a
32 hydrogen extraction process. Despite that, a considerable gap exists between
33 the growing interest in ammonia-based power applications and actually
34 available knowledge and understanding of physical and chemical
35 underpinnings of its oxidation process. In particular, the viability of
36 ammonia as an energy carrier rests on the overall conversion efficiency of
37 the process, including the ability to convert it at the necessary power levels
38 at the point of consumption with minimal environmental impact. Hence, the
39 research work behind this paper aims to bridge the gap between the
40 fundamental research and the development and implementation of ammonia
41 combustion technologies useful for cleaner, safe and sustainable energy
42 production systems.

43 Combining reactants dilution and preheating, realized by means of a strong
44 internal recirculation, a very peculiar combustion regime (MILD
45 Combustion) emerges. Potentialities of this regime, realized in a cyclonic
46 flow burner, to achieve stable ammonia combustion are explored accounting
47 for the influence of operative parameters. Dependence of process
48 stabilization and NO_x emissions on equivalence ratio, preheating
49 temperature and nominal thermal power of the inlet mixture is studied by
50 monitoring temperature and exhaust gases composition, with the aim of
51 identifying burner optimal operating conditions.

52 Results evidenced that for ammonia/air mixtures stable MILD combustion is
53 ensured. The burner has to operate under slightly rich conditions to
54 minimize NO_x emissions.

55

56 **Keywords:** Ammonia; Cyclonic Flow; Long residence times; MILD
57 Combustion; Stability

58 **1. Introduction**

59 The accomplishment of world energy demand has to deal with several
60 constrains that are rapidly and frequently changing near future energy
61 market possible scenarios. If global warming hastens the request of
62 renewable, green energy systems, on the other hand, geo-political and
63 economic equilibria anchor the energy production chain to well-established,
64 traditional energy production systems. This in turn hinders the drastic
65 reduction of greenhouse gas emissions to be achieved according to the strict
66 goals fixed over the years [1].

67 A point in common to most renewable energy sources (RES) is that their
68 location is resource dependent and effective distribution systems need to be
69 adapted and/or developed to accommodate this constraint. Another feature
70 of primary RES, like solar and wind, is their inherent intermittency and
71 variability both along the year (seasonality). With the expected expansion of
72 solar and wind based power generation, the major challenge will therefore
73 be to develop the national and regional grid structures and back-up systems
74 to ensure that security of supply remains high in spite of increased
75 variability of part of the supply sources. For this reason RES are often
76 identified as a major threat to the need of an energy uninterrupted supply
77 service [2]. There is a broad agreement that effective and affordable
78 methods for energy storage will be crucial in overcoming the inherent
79 intermittency of renewable resources and increasing their share of
80 generation capacity [3]. While efficient transmission and demand response
81 can offer a partial solution, a large number of mechanical, electrical,
82 thermal, and chemical methods have been developed for storing electrical
83 energy [4].

84 Among these methods, chemicals-based storage technologies offer the
85 advantage of being able to store large amounts of energy for long periods of
86 time. They also enjoy substantial design flexibility [5] and the
87 demonstration of the practical feasibility of synthetic fuels production and
88 utilization cycles on a global scale is a key enabling element in
89 decarbonizing also other sectors besides the power and district heating

90 sectors. A prominent role among those energy carriers is quite often
91 foreseen for use of hydrogen as an energy vector. However, issues
92 associated with storage and distribution are still barriers to its wide diffusion
93 [6].

94 On the other hand, following industrial interests, ammonia has been
95 recognized as a hydrogen carrier fuel [7] (hydrogen-density) and it burns
96 without carbon oxides emissions, being a carbon-free molecule, thus it
97 offers great potentialities to mitigate greenhouse gas emission [8].

98 Ammonia is the simplest representative of the nitrogen economy [9-10], and
99 also the second-largest synthetic commodity produced worldwide [11]. It
100 can be produced from renewable intermittent energy sources using available
101 technologies and plants [12]. A recent review article by Valera-Medina et al.
102 [13] showed that ammonia could provide for a practical next generation
103 system for energy transportation, storage and use for power generation, in
104 virtue of its established transportation network and high flexibility.

105 The International Energy Agency (IEA) has recently become a promoter of
106 ammonia for a carbon-free future. The Renewable Energy Division [14] has
107 observed that ammonia can be produced from renewable sources (wind,
108 solar, tidal, etc.), and in addition to redistribute hydrogen product from
109 electrolyzers connected to these systems. Ammonia is less costly to store for
110 a long time compared to hydrogen, and at least three times cheaper than this
111 one to ship on sea or land. Therefore, countries and international agencies
112 have started raising the awareness of the potential of ammonia for storage of
113 hydrogen, a rationale that has served to boost research in the area of its use
114 as energy vector and potential fuel.

115 However, earlier applications and studies of ammonia as a fuel reported
116 challenges associated with ammonia combustion [15].

117 However, straightforward ammonia utilization as a fuel, using a
118 conventional combustion process or technology does present much more
119 and greater issues and drawbacks than traditional hydrocarbon fuels do.

120 Ammonia has a burning velocity that is about five times lower than that of
121 methane, a narrow flammable range, a high minimum ignition energy and a
122 nitrogen atom in its molecule. In addition, ammonia/air flame temperature

123 (due to the lower LHV of ammonia) is lower and radiation heat transfer
124 from the flame is also lower than that of hydrocarbon flames because of the
125 absence of massive amounts of CO₂ in the exhaust. These drawbacks may
126 eventually result in a low heat release rate and low rate heat transfer that can
127 compromise the flame stabilization process, leading to low combustion
128 efficiency [16].

129 In order to overcome the limitations imposed by ammonia chemical
130 properties, the common strategy is to stabilize the process using a “fuel
131 enhancer”, but particular care has to be devoted to NO_x emissions.

132 Meyer et al. [17] stabilized the oxidation process of ammonia in a 40 kW
133 burner using hydrogen and methane. They showed that the use of a flame
134 holder increased the combustion efficiency, with an appreciable reduction in
135 NO_x emissions. Species recombination (NO_x and unburned ammonia) has
136 been suggested as a possible explanation of the evidence.

137 The Fukushima Renewable Energy Institute (FREA) has developed fuel
138 flexible platforms to burn liquid NH₃ produced from renewable sources, in
139 combination with kerosene in a 50 kW micro-gas turbine. A selective
140 catalytic converter (SCR) was used to reduce the NO_x emissions down to an
141 acceptable value [18].

142 The work made at Tohoku University burned a mixture of ammonia and
143 kerosene. demonstrated that as the mixture equivalence ratio for different
144 methane-ammonia blends increases towards stoichiometry, unburnt species
145 such as NH₃, CO and total hydrocarbons decrease in contrast to NO_x. Due to
146 the difficulties to attain a satisfying efficiency together with an acceptable
147 level of emission (mainly NO_x) using a single-stage combustor, a two-stage
148 combustion system, with a better mixing between recirculating gases from
149 reaction regions and fresh gases, has been designed and tested. Preliminary
150 results suggest that higher emissions performance can be attained with this
151 configuration (lower NO_x and unburnt gas species emissions) while
152 maintaining high combustion efficiencies [19].

153 Valera-Medina et al. [20] presented a series of studies burning mixture of
154 ammonia and hydrogen/methane at different concentrations in a swirl
155 burner. Results showed the complexity of stabilizing premixed ammonia

156 blends. NO_x and CO were considerably lower at equivalence ratios higher
157 than 1.10. Authors hypothesised the onset of a region of chemically reactive
158 balance between methane/hydrogen and ammonia combustion, with
159 recombination of NO_x with unburned ammonia, increasing OH radicals.
160 Unfortunately the degree of knowledge is not yet sufficient to give a
161 definitive explanation to the observed phenomenology.
162 Similar studies on combustion characteristics of mixtures of ammonia and
163 other fuels (hydrogen and diesel) in an internal combustion engines were
164 made by Reiter and Kong [21].
165 It is worthwhile concluding here that, in spite of the several efforts made in
166 few past years and of the growing interest in ammonia-based power
167 applications, the scientific literature on the topic is still scarce, and the
168 current degree of knowledge still needs significant research efforts to enable
169 optimal design procedures.
170 The required technology to deliver this so-called “green NH_3 fuel” vision
171 (<https://nh3fuelassociation.org>) has been only demonstrated at rather small
172 scales. Further studies at a larger scale, including the integration of
173 technology within the complete energy cycle, are still needed.
174 According to the general picture, features and potential
175 advantages/drawbacks of using ammonia as fuel in advanced combustion
176 technologies for stationary power generation, such as MILD [22], Colorless
177 Distributed Combustion (CDC) [23-25] or High Temperature Air
178 Combustion [26], are also largely unknown. As matter of facts, to the best of
179 the authors’ knowledge, there are no studies in the literature that has shown
180 the feasibility and stability of such combustion processes when pure
181 ammonia is used as fuel.
182 Hence, the aim of this paper is to provide an insight into these practical
183 issues, utilizing a cyclonic flow burner operated in MILD Combustion
184 conditions, investigating ammonia-firing conditions.
185 The stabilization of the reactive process was investigated and the influence
186 of operative parameters (preheating temperature, equivalence ratio and
187 thermal power) on the system performance is also explored for stationary
188 applications. Thus, this paper helps to bridge the gap between research,

189 development and implementation for an innovative technology which has
190 the potential to provide a sustainable energy system.

191 **2. Experimental setup and methodology**

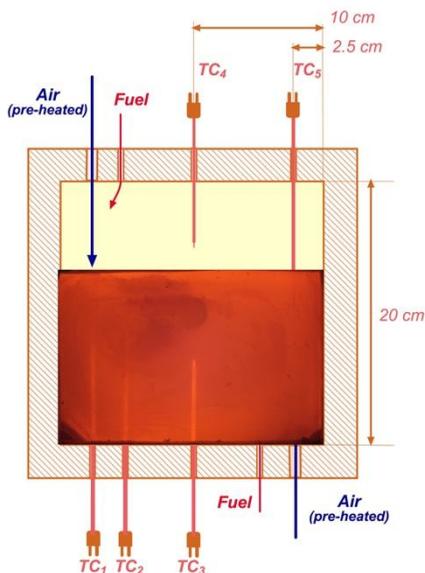
192 The experimental campaign was carried out in the Laboratory Unit
193 CYclonic (LUCY) burner [27, 28] reported in the sketch of Figure 1. It
194 consists of an alumina prismatic chamber ($20 \times 20 \times 5 \text{ cm}^3$) externally covered
195 with a heat-insulating material. It is located inside an AISI 310s stainless
196 flanged case that can be easily opened for inspection operations. The
197 stainless-steel top is provided of a rectangular opening, hosting a quartz
198 window for visual observation and other diagnostics. Several shielded
199 thermocouples (type N) are used to monitor the combustion process. One
200 thermocouple is placed at the exit of the burner and five thermocouples at
201 the mid-plane of the chamber. Two central thermocouples (TC_3 and TC_4),
202 one intermediate (TC_2) and two lateral ones (TC_1 and TC_5) are located at
203 10 cm, 5 cm and 2.5 cm from the lateral wall, with a protrusion length of
204 5 cm, 7.5 cm and 10 cm respectively.

205 Fig. 1 shows a sketch of the top-view of the combustion chamber with a
206 picture of the typical operational behavior under flameless combustion
207 mode, monitored through the quartz window.

208 The cyclonic flow-field within the chamber is obtained through two couples
209 of anti-symmetrically injectors, used for fuel and oxidizer streams, with ID
210 of 1.5 mm and 8 mm, respectively. The flow injection configurations and
211 the position of the exit (in the center of the bottom face of the chamber)
212 induce a toroidal flow-field. Flow rates can be easily changed in a wide
213 range, resulting in a nominal thermal power (P) from 0.1 up to 10 kW.

214 The oxidizer flows are preheated by means of two heat exchangers (see Fig.
215 2 of Ref. 27) to the desired inlet temperature (up to 1200 K) (T_{in}) before
216 entering the reactor. Fuel is fed into the combustion chamber at
217 environmental temperature. The burner is located within electrical ceramic
218 fiber heaters to minimize heat exchange towards the surroundings.

219 The mixture inlet equivalence ratio can be easily changed (from ultra-lean to
220 very rich conditions) to investigate the effect of mixture composition on the
221 oxidation behavior.



222
223 *Figure 1 Picture of the burner operating under Ammonia Flameless*
224 *combustion superimposed to a sketch of the cyclonic*
225 *combustion chamber with some geometrical features.*

226 The exhaust gases are sampled from the central outlet by a cooled probe and
227 are analyzed through a portable Agilent micro-GC analyzer that allows to
228 measure volumetric concentrations of O₂, H₂, N₂.

229 NO and NO₂ are measured by means of both a flue gas analyzer (TESTO
230 350) and a dedicated ABB analyzer.

231 In addition, also ammonia slip was monitored by measuring the
232 concentration of NH₃ at the exit, separately with respect to NO_x. Gastec
233 detection tubes (Gastec Corporation) was used to measure NH₃ emissions in
234 exhaust gas. During the experiments, measurements were repeated at least
235 three times for each condition to ensure good repeatability of the
236 experimental data obtained. Every single test was conducted for about 20
237 min.

238 NO_x, NH₃ and H₂ concentrations are normalized to 15% O₂.
239 Further details of the experimental apparatus are reported in previous
240 publications of the same research group [27, 29].

241 **3. Results and discussions**

242 The experimental campaign was carried out by operating LUCY burner with
243 ammonia/air mixtures at atmospheric pressure. The performance of the
244 cyclonic burner has been characterized in terms of system working
245 temperatures (T) and pollutant emissions (NO_x) for several values of the
246 mixture equivalence ratio (Φ), in accordance with previous works [27]. Both
247 the inlet preheating temperature and thermal power were parametrically
248 changed.

249 In particular, Φ was varied from fuel very lean ($\Phi = 0.4$) to very rich ($\Phi =$
250 1.8) values in order to investigate the performance in a wide range of
251 working conditions.

252 Finally, emissions of trace components (NH₃, H₂) at the stack were also
253 reported for some operative conditions.

254 **3.1 Influence of the inlet preheating level (T_{in})**

255 First, experimental tests were realized for three values of the inlet preheating
256 level (300 K, 600 and 900 K) and for a fixed value of the nominal thermal
257 power $P=5$ kW, as a reference value for efficient working conditions
258 identified in previous works with several hydrocarbon fuels [25, 30]. The
259 analysis was extended to three values of the thermal power (4, 5 and 7 kW)
260 for a fixed inlet temperature.

261 Results suggested that MILD conditions are ensured also for low load
262 values due to the strong internal recirculation of burned products that
263 stabilizes locally a distributed ignition. The uniformity of the temperature
264 field was verified for each experimental test and the maximum difference
265 between thermocouples was 30 K. The working temperature reported in the

266 following sections was evaluated as the mean value between TC₃, TC₄ and
267 TC₅.

268 Figure 2 shows the mean system working temperature (T) and the
269 characteristic residence times of the mixture (τ) by varying the equivalence
270 ratio.

271 The characteristic average residence times (τ) was obtained for each
272 condition by scaling the mean residence time computed in non-reactive
273 conditions with the average temperature in the chamber.

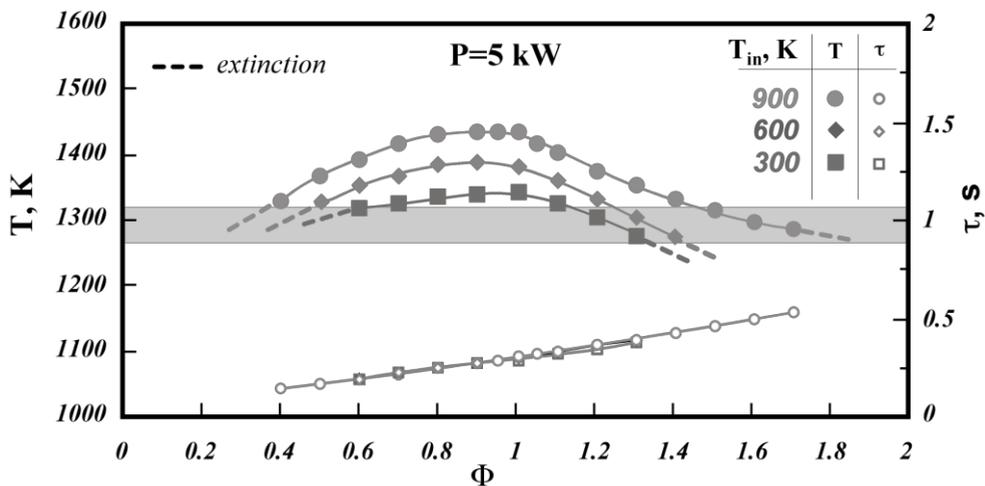
274 As it is possible to note from Figure 2, the sustainability of the combustion
275 process is ensured at 5 kW when the working temperature is higher than
276 about 1250 K in the whole range of inlet preheating temperature and
277 equivalence ratio here investigated. Working temperatures lower than
278 1300 K (dashed lines) should be avoided because of the occurrence of
279 extinction phenomena with high emissions of unburned products (namely
280 H₂).

281 The dashed lines and the grey area identify feeding conditions where global
282 extinction behaviors were observed. The extinction strongly depends on the
283 equivalence ratio and slightly varies as a function of both the inlet
284 preheating level and thermal power.

285 Thus, a unique reactor extinction range was identified as indicated by the
286 grey area in Fig. 2.

287 Such an extinction behavior was recognized in the same burner in previous
288 works of the same group for methane and propane mixtures [31] where the
289 oxidation process was found to be stable when the temperature inside the
290 reactor was above 1050 K. Thus, it was possible to identify a unique cross-
291 over temperature for the ignition/extinction phenomena that is mainly
292 related to the kinetic stabilization of the reactive structure. In case of
293 gaseous hydrocarbon paraffinic fuels, this temperature corresponds to the
294 activation temperature of the high temperature branching mechanism. As
295 found from a spectrum of observations in various flame configurations and
296 from several descriptions of hydrocarbon combustion, this transition toward
297 stabilized reactive conditions may be related to the dominance of chain-
298 branching reactions at high temperatures [32].

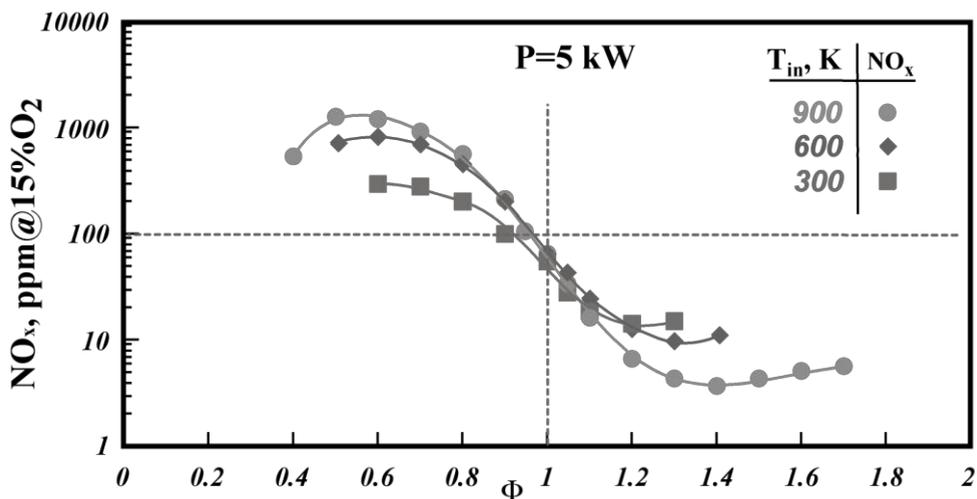
299 Noticeably, such threshold is higher in the case of ammonia-air MILD
 300 combustion and therefore it could be stated that this behavior is related to
 301 the switch on high temperature kinetic branching of ammonia chemistry.
 302 The maximum burner working temperature is reached around the mixture
 303 stoichiometric value ($\Phi = 1$) for all the inlet preheating temperatures here
 304 investigated. In particular, it reaches the highest values for $T_{in} = 900$ K. The
 305 maximum working temperature is around 1320 K without preheating the
 306 inlet flows ($T_{in} = 300$ K), while it is 1470 K for an inlet temperature of 900
 307 K.
 308 Thus, Figure 2 shows that the range of stable operating conditions in terms
 309 of equivalence ratio is widened by increasing the preheating level of the
 310 inlet air-flow. In particular, at environmental conditions ($T_{in} = 300$ K) a
 311 stable oxidation process has been obtained in the range $0.6 < \Phi < 1.3$,
 312 whereas by preheating the inlet oxidizer flow up to $T_{in} = 900$ K the system
 313 allows to achieve stable conditions in a wider Φ interval ($0.4 < \Phi < 1.7$).



314
 315 *Figure 2 Working temperature (T) and characteristic residence time (τ)*
 316 *for ammonia-air mixtures as a function of Φ for several T_{in}*
 317 *values at $P = 5$ kW.*

318 On the other hand, the characteristic residence time (τ) reported in Figure 2
 319 ranges from $\tau = 0.1$ s to $\tau = 0.55$ by increasing the mixture equivalence ratio

320 from 0.4 to 1.7. The same values have been obtained for all the preheating
 321 inlet temperature here investigated.
 322 Figure 3 reports NO_x emissions for the same condition ($P = 5 \text{ kW}$) by
 323 varying the equivalence ratio of the mixture, parametrically in the inlet
 324 preheating temperature.
 325 In particular NO_x emissions under lean conditions for $\Phi = 0.6$, ranged from
 326 250 ppm without preheating the oxidizers, to 1000 ppm for $T_{\text{in}} = 900 \text{ K}$.
 327 As expected, it is possible to observe that NO_x emissions significantly
 328 decrease moving toward fuel rich conditions for all cases here investigated.
 329 In particular, they decrease of about one order of magnitude ($\text{NO}_x < 100$
 330 ppm) when passing from fuel-lean to stoichiometric mixtures. The
 331 horizontal dashed line in Fig. 3 is related to the 100 ppm value.
 332



333
 334 **Figure 3** NO_x emissions for ammonia-air mixtures as a function of Φ for
 335 several T_{in} values at $P = 5 \text{ kW}$.

336 Figure 3 shows that levels of NO_x in lean ammonia-air MILD Combustion
 337 is slightly dependent on the preheating level. Thus, the stoichiometry is seen
 338 to have a major impact on the NO_x formation. Based on information present
 339 in literature, oxidation of NH_i by O , H and OH radicals leads to NO
 340 production through the HNO intermediate under lean conditions [33].

341 As qualitative behavior, such results are in agreement with literature on
342 ammonia-air combustion in model reactors or gas-turbine combustors [34-
343 37]. It is worth to note that the strong relevance of results reported in this
344 paper relies on the absolute concentration of NO_x which is very low with
345 respect to the NO_x concentration generally produced in other systems during
346 ammonia oxidation. Indeed, it is the first time that the pure ammonia
347 oxidation has been stabilized in stoichiometric condition (vertical dashed
348 line in Fig. 3) corresponding to a NO_x concentration of 70 ppm.

349 As expected, the minimum NO_x emission levels are obtained when the
350 burner is operated with rich mixture compositions. Indeed, the system
351 reaches single-digit values for slightly-rich mixtures ($\Phi > 1.1$). In this
352 conditions, reactions involving NH_2 and N_2H_2 have a key role in the NO_x
353 reduction. Specifically, the reactions of $\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$,
354 $\text{NH} + \text{NO} \rightarrow \text{NNH} + \text{OH}$ were shown to have a great effect on the
355 decomposition of NO_x at all preheating temperatures of the reactants, which
356 results in an extremely low NO formation rate, indicating the potential to
357 reduce NO_x formation in NH_3 combustion [38].

358 Finally, it is also worth to note that the NO_x reduction equivalence ratio
359 range is compatible with the temperature window for the Thermal De NO_x
360 process ($1250 \text{ K} < T < 1400 \text{ K}$) [39, 40].

361 The consideration pointed out for lean conditions applies also for the fuel-
362 rich conditions. It is the first time that the pure ammonia combustion has
363 been stabilized in slightly rich-conditions with a NO_x emission in 1-digit
364 range.

365 The results reported in Figure 3 show that high values of the inlet preheating
366 temperature of the air flow allows to lowering NO_x emissions at 3 ppm
367 when the system is operated with rich mixtures, while the opposite effect is
368 obtained if the burner works under lean conditions ($\Phi < 0.9$), obtaining NO_x
369 levels of about 1000 ppm. This suggests that the best performance in terms
370 of NO_x emissions can be obtained in the operational window from
371 stoichiometric to slightly-rich conditions ($1 < \Phi < 1.2$).

372

3.2 Influence of the nominal thermal power (P)

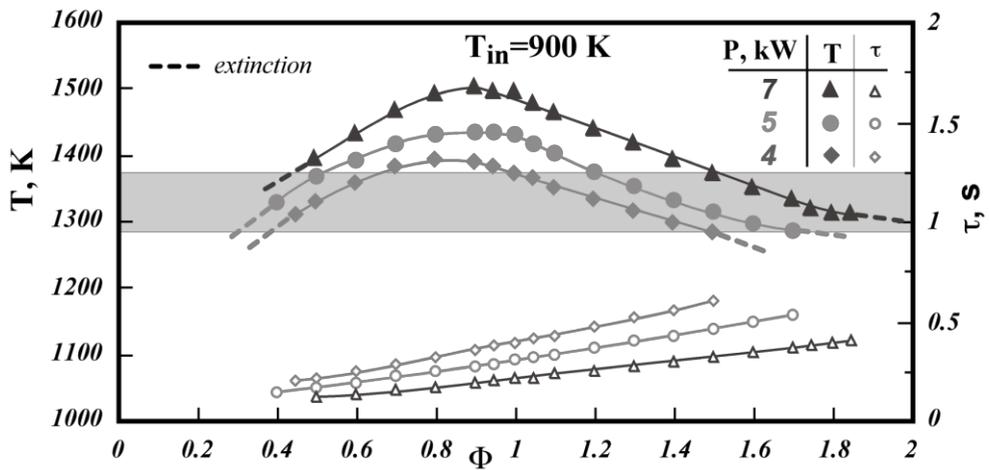
373 Further experimental campaigns have been carried out in order to evaluate
374 the performance of the cyclonic burner by varying the nominal thermal
375 power of the system for a fixed value of the preheating temperature of the
376 air-flow.

377 Experimental tests were realized for three values of nominal thermal power
378 by keeping the inlet temperature of the air-flow at the highest level ($T_{in}=900$
379 K). In fact, this value of T_{in} permits to ensure the lowest NO_x levels.

380 Figure 4 shows the results in terms of working temperatures and
381 characteristic residence time at $T_{in} = 900$ K by varying the equivalence ratio
382 of the ammonia-air mixture, for three values of the nominal thermal power P
383 (4,5 and 7 kW).

384 As reported in Figure 4, the maximum working temperature is reached
385 around the stoichiometric point for all the values of the nominal thermal
386 power here considered, as expected. In particular, the working temperature
387 ranged from $T = 1300$ K to $T = 1400$ K at $P = 4$ kW in the operational
388 window of the equivalence ratio from $\Phi = 0.45$ to $\Phi = 1.5$ until the
389 extinction behavior occurs.

390 When the system is operated at $P = 5$ kW the working temperature ranged
391 from $T = 1300$ K to $T = 1450$ K for $0.4 < \Phi < 1.7$. A further increase of the
392 thermal power up to $P = 7$ kW allows to obtain working temperatures
393 ranging from $T = 1300$ K to $T = 1520$ K in the operational window of the
394 equivalence ration from $\Phi = 0.5$ to $\Phi = 1.8$. It is worth to note that for each
395 thermal power here considered the extinction phenomena was obtained
396 when the system temperature falls in the narrow interval with $1300 \text{ K} < T <$
397 1400 K .



398

399 **Figure 4** Working temperature (T) and characteristic residence time (τ)
 400 for ammonia-air mixtures as a function of Φ for several P
 401 values at $T_{in} = 900$ K.

402 On the other hand, characteristic residence times (τ) rise with the
 403 equivalence ratio according to the lowering of the mixture inlet flows.
 404 Moreover, characteristic residence times are the highest for the minimum
 405 value of the thermal power, ranging from $\tau = 0.3$ to $\tau = 0.7$ s at $P = 4$ kW
 406 and from $\tau = 0.2$ to $\tau = 0.45$ s at $P = 7$ kW.

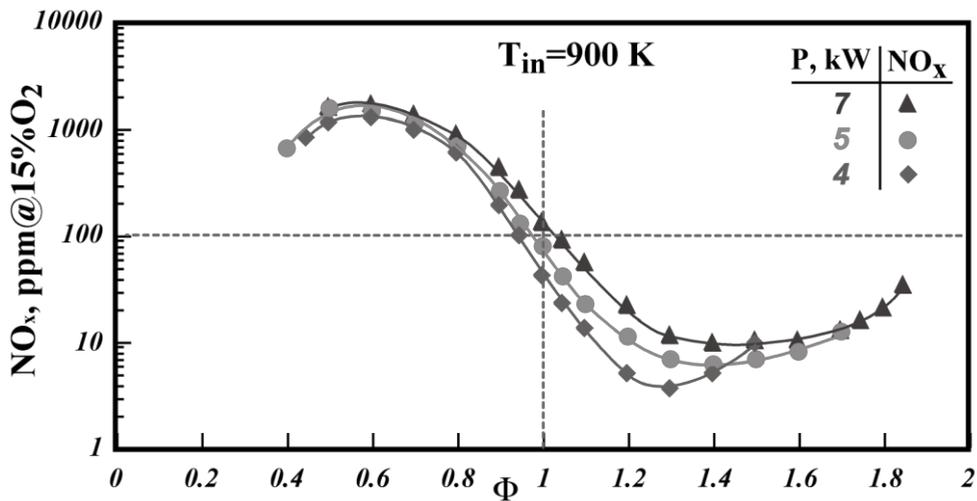
407 The prolongation of residence times at lower thermal power influences the
 408 NO_x reduction efficiency [41].

409 In fact, Figure 5 shows NO_x emissions at fixed $T_{in} = 900$ K by varying the
 410 equivalence ratio of the mixture Φ for the three values of the nominal
 411 thermal power here considered.

412 As shown in Figure 5, NO_x emissions are very high, up to 1000 ppm
 413 independently from the thermal power, when the system is operated with
 414 very lean mixtures ($0.4 < \Phi < 0.8$).

415 In accordance with the results reported before, minimum NO_x emissions
 416 have been obtained when the cyclonic burner is operated with slightly-rich
 417 mixtures and the trends are the same independently from the thermal power.

418



419

420 **Figure 5** *NO_x emissions for ammonia-air mixtures as a function of Φ for*
 421 *several P values at $T_{in} = 900$ K.*

422 Specifically, when the equivalence ratio is higher than 1.1 and the
 423 preheating temperature is 900 K it is possible to operate the system in single
 424 digit for the case at P=4 kW. They are in the range $10 < NO_x < 100$ ppm for
 425 higher thermal power levels.

426 Minimum NO_x emissions are 9 ppm at $\Phi = 1.5$ when the cyclonic burner is
 427 operated at P = 7 kW and they are increased at 80 ppm at $\Phi = 1$. The lowest
 428 NO_x emissions of 3 ppm at $T_{in} = 900$ K have been obtained at P = 4 kW with
 429 a mixture equivalence ratio of $\Phi = 1.3$. Thus, the minimum NO_x shifts
 430 toward lower equivalence ratio values by decreasing the nominal thermal
 431 power of the system.

432 It is worth to note that, also in this case the burner exhibits NO_x emissions
 433 that are equal or lower than 100 ppm (horizontal dashed line in Fig. 5) at the
 434 stoichiometric point (vertical dashed line). Furthermore, low thermal powers
 435 (4 kW) with high preheating levels permits to perform the cyclonic burner
 436 close to the single digit level and such emissions are increased for higher
 437 thermal power.

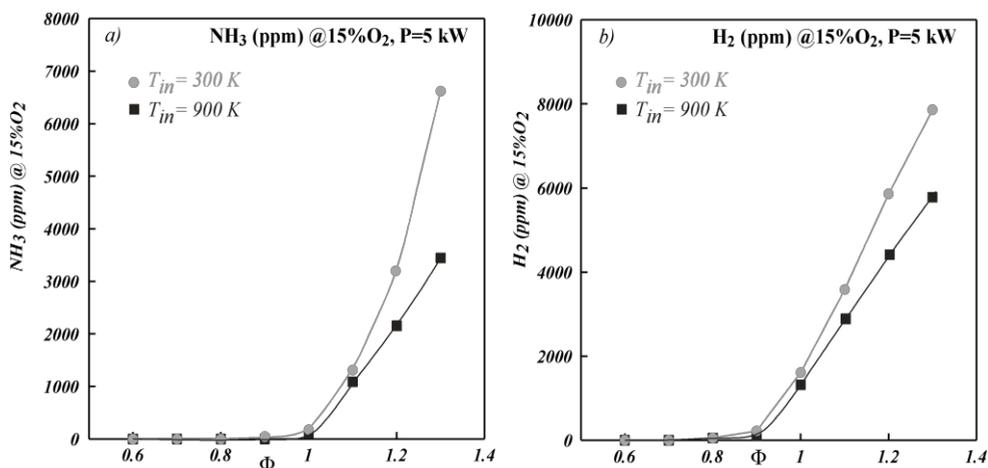
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3.3 NH₃ and H₂ emission characteristics

439 In order to thoroughly characterize the performance of the system, NH₃ and
 440 H₂ concentrations at the exit of the cyclonic burner were also reported,
 441 normalized at 15% O₂.

442 Figure 6 shows the experimental value of NH₃ slip and produced H₂ for a
 443 fixed thermal power of 5 kW and for two values of the inlet preheating level
 444 (300 and 900 K). For lean conditions, NH₃ (Fig. 6a) emissions were almost
 445 zero. In particular, at $\Phi=0.9$ they are 6 ppm for $T_{in}=900$ K whereas they
 446 reach 29 ppm when the inlet temperature is decreased at 300 K. For
 447 stoichiometric conditions ($\Phi=1$), the measured NH₃ concentration is around
 448 100 ppm at $T_{in}=900$ K while it is increased at 168 ppm at ambient inlet
 449 temperature.

450



451

452 **Figure 6** NH₃ (a) and H₂ (b) volumetric emissions (ppm@15%O₂) for
 453 ammonia-air mixtures as a function of Φ for $P= 5$ kW and two values of T_{in}
 454 (300 K, 900 K).

455

456 For fuel-rich conditions, the NH₃ concentration is rapidly increased by about
 457 one order of magnitude (1070 ppm) at $\Phi=1.1$ for $T_{in}=900$ K and it reaches
 458 1320 ppm when T_{in} is 300 K. When the equivalence ratio was larger than
 459 1.1, the NH₃ concentration steeply increases with Φ and reached 3000 ppm

460 at $\Phi=1.3$ for $T_{in}=900$ K, whereas it is 6600 ppm for $T_{in}=300$ K.
461 On the other hand H_2 emissions are not negligible for slightly fuel-lean
462 conditions ($\Phi=0.9$), reaching 114 and 210 ppm for $T_{in}=900$ K and 300 K,
463 respectively.
464 At the stoichiometric equivalence ratio H_2 is around 1500 ppm for the two
465 values of T_{in} and it increases up to 6000 ppm when $\Phi=1.3$ at $T_{in}=900$ K. H_2
466 increases at 8000 ppm at $\Phi=1.3$ when the inlet preheating level is decrease
467 at the ambient temperature.
468 Thus, NO_x and NH_3 concentrations were almost of the same order of
469 magnitude (around 100 ppm) at $\Phi=1$ and very low in comparison with
470 concentrations obtained in other combustion systems. Of course, further
471 improvement can be obtained with a simultaneous reduction of NO_x and
472 NH_3 coupling the use of stoichiometric mixtures in a practical NH_3 -fueled
473 combustor with selective catalytic reduction (SCR) systems.

474 **4. Conclusions**

475 In this paper, the stabilization of ammonia MILD Combustion in a wide
476 range of parameters was demonstrated and discussed for the first time. It
477 was shown that very interesting NO_x concentration and NH_3 characterize the
478 ammonia oxidation in the condition considered.

479 The main operational characteristics of ammonia/air combustion in a
480 cyclonic burner were investigated through temperature and exhaust gas
481 emission measurements. Results of the influence of main external operating
482 parameters, such as equivalence ratio, inlet preheating level and nominal
483 thermal power on system performance were presented. The appearance of
484 flameless combustion conditions and the temperature values were used to
485 investigate the stability characteristics.

486 In particular, MILD Combustion regime was achieved for a wide range of
487 external parameters with reduced combustion peak temperatures and very
488 low NO_x emissions in a wide operational window.

489 The internal recirculation induced by cyclonic flow-field allows for the
490 establishment of MILD combustion also with ammonia as fuel with very

491 good performance in terms of pollutant emissions, confirming the very high
492 fuel flexibility of the system. This gives new insight into the technological
493 applications of such combustor; in fact, in the author's knowledge there are
494 no studies in the literature that has shown the feasibility of MILD
495 Combustion when pure ammonia is used as fuel for small-scale burners.
496 Remarkable performance in terms of stabilization of the oxidation process
497 and low pollutants has been verified in a wide range of operating conditions.
498 The sustainability of the combustion process with ammonia is ensured when
499 the working temperature is higher than about 1250 K for each condition
500 investigated in this manuscript. Working temperatures lower than 1300 K
501 should be avoided because of the occurrence of extinction phenomena with
502 high emissions of unburned products.
503 In particular, the present work permits to identify a narrow reactor
504 extinction range ($1250 < T < 1350$ K) also recognized in previous works for
505 hydrocarbons combustion. The threshold is higher in the case of ammonia-
506 air MILD combustion since it is related to the switch on high temperature
507 kinetic branching of ammonia chemistry.
508 It is noteworthy that NO_x are significantly lower than the typical
509 concentrations measured in standard combustion processes in the whole
510 range of experimental parameters considered. More specifically, the
511 measured NO_x levels lower than 100 ppm open a clear opportunity to use
512 ammonia as fuel in MILD Combustion conditions. In this sense the best
513 operational window in order to minimize NO_x emissions spans from slightly
514 fuel-lean to fuel-rich conditions.
515 The preheating the inlet air-flow allows to reach very low NO_x emissions
516 also for stoichiometric mixtures, while for lean mixtures lower emissions
517 have been obtained without external preheating.
518 Despite that, when NO_x emissions are minimized some unburned
519 components are obtained in fuel-rich conditions, especially with respect to
520 NH_3 and H_2 . In particular, when the inlet equivalence ratio is higher than 1.1
521 the NH_3 concentrations are higher than 1000 ppm. SCR techniques could be
522 used to further decrease both the NO_x and NH_3 emissions with equivalence

523 ratios in the interval between 1 and 1.1. Inlet preheating level play an
524 important role also with respect to unburned ammonia emissions.
525 Finally, the system performance was investigated also in terms of load
526 following and in particular for higher thermal powers the minimum NO_x
527 shifts toward higher equivalence ratios, according to the lowering of the
528 maximum working temperatures.

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