Full Length Article

NH$_3$ oxidation and NO reduction by NH$_3$ in N$_2$/Ar and CO$_2$ atmospheres

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A B S T R A C T

Impact of using CO$_2$ or N$_2$/Ar as bath gas, representative respectively of oxy-fuel or air combustion scenarios, has been evaluated on the oxidation of ammonia under a variety of operating conditions in a combined experimental and simulation study. Variables of relevance as temperature and oxygen stoichiometry have been considered at atmospheric pressure and under carefully controlled experimental conditions. Additionally, the impact of the presence of NO, which can be formed from ammonia oxidation, has also been evaluated. The experimental results obtained have been simulated with significant success with a detailed literature kinetic mechanism, which has been further used to interpret the main experimental observations. The results obtained are of interest in the power and energy industry, and can be used for guiding the co-firing of NH$_3$ and carbon containing fuels.

1. Introduction

Ammonia conversion under combustion conditions has become a major topic of research, mainly because of its interest as a carbon free fuel [e.g.,1–8]. Ammonia can also be generated as an intermediate product in conversion of coal, biomass and other fuels containing nitrogen [e.g.,9]. While ideally ammonia combustion will generate molecular nitrogen and water vapor as reaction products, practical devices may run far from ideality and thus contribute to the generation of nitrogen oxides, mainly NO, depending on the operating conditions [e.g.,1,3,5,10,11]. Additionally, the use of different combustion strategies, such as oxy-fuel combustion, may affect the oxidation regimes of ammonia and the formation of pollutant species.

The presence of high amounts of CO$_2$, as found in oxy-fuel combustion and biogas combustion, can lead to significant differences in the oxidation behavior of species. Studies dealing with oxidation of HCN [12], HCN-NO [13], NH$_3$ [14] or NH$_3$-CH$_4$ [15,16] under oxy-fuel combustion conditions have shown an important influence of the presence of CO$_2$ for the conversion of nitrogen species. The presence of CO$_2$ has been reported to affect the concentration and speciation of the O/H radical pool [e.g.,17], since CO$_2$ competes with O$_2$ for atomic hydrogen through the CO$_2$ + H $\rightleftharpoons$ CO + OH reaction (r1). Reaction r(1) reduces the formation of chain carriers by the O$_2$ + H $\rightleftharpoons$ O + OH reaction (r2), thus affecting the conversion of reactants.

Few works about ammonia oxidation in a CO$_2$ atmosphere and the comparison of the results obtained in CO$_2$ and N$_2$/Ar environments are presented in the literature. A recent jet-stirred reactor study of oxidation of syngas-ammonia mixtures in N$_2$ and CO$_2$ atmospheres, respectively, has concluded that presence of CO$_2$ affects the conversion of ammonia [18]. It was found that the reactant consumption was delayed and more CO is produced in high CO$_2$ concentration, and that under these high CO$_2$ concentration conditions, fuel-NO formation is suppressed in fuel-lean conditions, while the fuel-NO production is significantly enhanced in fuel-rich conditions. The results are consistent with those of a recent flow reactor study by our group [14], in which experiments under stoichiometric conditions in a CO$_2$/Ar atmosphere were conducted. In that work, the presence of CO$_2$ was identified to slow down the conversion of ammonia as the temperature is increased, and revealed a complex behavior attributed to the presence of high CO$_2$ concentration.

Additionally, since NO is produced from ammonia oxidation, the study of interaction of NH$_3$ and NO is of interest. Selective non-catalytic reduction of NO (SNCR) by ammonia is a well-known process [e.g.,19–24], but the impact of a high CO$_2$ concentration, such as that occurring in oxy-fuel combustion, may affect the interaction of the nitrogen species (NO and NH$_3$).

In this context, this work shows new results and conclusions that complement those few available in the literature, by bringing new experimental results obtained in a plug flow reactor. Specifically, it addresses the effect of a CO$_2$ environment, representative of oxy-fuel combustion conditions or the use of mixtures of ammonia and biogas, compared to an O$_2$/N$_2$ or O$_2$/Ar environment, representative of conventional combustion, on the conversion of ammonia. Furthermore, the impact of the presence of NO, both related to conversion of ammonia

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and to the minimization of this pollutant, is considered in a CO_2 atmosphere and compared to the conventional N_2 combustion scenario. A novelty of the present results also includes the use of argon instead of nitrogen to balance the experiments, in order to be able to analyze the formation of N_2 with precision. This work provides also new experimental data obtained under carefully controlled conditions and that are useful for chemical model validation of NH_3 combustion, which is of interest in the power and energy industry.

2. Experimental methodology

Table 1 shows the conditions of the different experiments. The experiments are performed in a flow reactor installation described elsewhere [e.g.,14,25]. Reactants (NH_3, NO, and O_2), diluted either in a CO_2/Ar or a N_2 or Ar atmosphere, are fed from gas cylinders through mass flow controllers. Experiments with CO_2 are representative of oxyfuel combustion conditions while experiments with N_2 and/or Ar would be representative of conventional air combustion systems. In the experiments in the presence of NO, Ar has been used as bath gas to make possible a quantification of N_2 formed from ammonia and allowing for an N-balance. No significant influence of using Ar compared to N_2 has been found in experiments dealing with NH_3 conversion under otherwise similar conditions [26]. Water is added by saturating a nitrogen or argon stream in water. The gases are fed to the quartz tubular flow reactor in four separate streams following the procedure of Alzueta et al. [27,28]: NH_3, NO and O_2 are fed through individual injectors and mixed at the inlet of the reaction zone with a stream containing N_2, Ar and/or CO_2. The quartz flow reactor of 0.87 cm internal diameter and 20 cm of length is heated by a three-zone electrical oven, allowing an isothermal reaction zone where temperature is kept constant within ± 5 K. Reaction is quenched at the outlet of the reactor by means of external air addition. At the outlet of the reactor, the product gas is analyzed using a gas micro-chromatograph equipped with TCD detectors for NH_3, O_2, H_2, N_2 and N_2O quantification (NH_3 and N_2O are analyzed in a CP-volamine column and O_2, H_2 and N_2 in a MS5A column), and four continuous infra-red analyzers for NH_3, NO, NO_2, and N_2O. For selected experiments, an FTIR spectrometer is used to detect the possible presence of additional species. The uncertainty of the measurements is estimated to be 5 %, and not less than 5 ppm for the continuous analyzers and 10 ppm for the TCD detectors and the FTIR spectrometer [1].

Pressure is atmospheric and the temperature is varied in the 700–1450 K range. The total flow rate is 1 L (STP)/min, resulting in a gas residence time (t_r) as a function of temperature, as shown in the experiments description of Table 1. The stoichiometry (λ) is defined as the quotient between the oxygen available for reaction and the stoichiometric oxygen, in the following reaction:

$$NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O \tag{r3}$$

Experimental sets 1 to 4 and 5 to 8 correspond to similar experiments in which the stoichiometry is changed from fuel-rich ($\lambda = 0.33$) to lean conditions ($\lambda = 3.33$), carried out in either a N_2 atmosphere (1–4) or a CO_2/Ar atmosphere (5–8). Additionally, the impact of the presence of around 1000 ppm NO is explored in experiments 10 to 13 and 14 to 17 in Ar and CO_2/Ar atmospheres, respectively, and varying stoichiometry from fuel-rich to very lean conditions.

3. Kinetic modelling

Simulations have been performed with a literature mechanism. The mechanism used in the present calculations was compiled in an earlier work [28]. It was based in the mechanism by Glarborg et al. [24] which was updated for ammonia, diazene and amines chemistry [26,29–32]. Apart from the conversion of NH_3 reaction subset, the mechanism used also includes submechanisms for C1-C2 hydrocarbons [33–35], amines [23], cyanides [36], hydrocarbon/nitrogen interactions [16,37] and an acetonitrile reaction subset [38]. The full mechanism (kinetic and thermodynamic data) is included as supplementary material.

Calculations have been performed using the PFR model of the Chemkin-Ansys sofware [39]. The rate constants for the reverse reactions were computed from the forward rate constants and the equilibrium constants using the thermodynamic data from the same sources as the kinetic mechanisms.

4. Results and discussion

4.1. NH_3 oxidation

Fig. 1 (a,b,c,d) shows, for the stoichiometries considered ($\lambda = 0.33$–3.33), the experimental (symbol) and simulated (lines) results of the concentrations of NH_3 and NO both in CO_2 and N_2 atmospheres as a function of temperature.

The NH_3 concentration profiles are shifted slightly to lower temperatures as the stoichiometry increases, for both O_2/CO_2 and O_2/N_2 or O_2/Ar atmospheres, in agreement with the general knowledge on ammonia conversion that a higher availability of oxygen boosts ammonia conversion to lower temperatures [e.g.,1,3,14,24]. The effect of stoichiometry is comparatively higher for the N_2/Ar combustion atmosphere. For a given stoichiometry, the conversion of NH_3 starts to occur at a lower temperature in the N_2 atmosphere and the higher conversions are kept along the whole temperature range considered, with conversion of ammonia being complete at lower temperatures as the O_2 concentration is higher. However, the oxidation of ammonia in the CO_2 atmosphere appears to be lower for the stoichiometries studied.

Table 1
Experimental conditions. pw denotes present work.

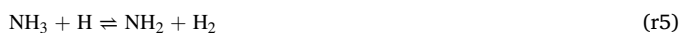| Set	NH_3 (ppm)	NO (ppm)	O_2 (ppm)	H_2O (%)	Ar (%)	CO_2 (%)	N_2 (%)	λ	t_r (s)	Source
1	1020		255	0.6	0	0	99.27	0.33	195/T(K)	pw
2	1008		882	0.6	0	0	99.21	1.17	195/T(K)	pw
3	1091		1364	0.6	0	0	99.17	1.67	195/T(K)	pw
4	1050		2625	0.6	0	0	99.05	3.33	179/T(K)	pw
5	923		231	0.6	25	74.28	0	0.33	195/T(K)	[14]
6	906		793	0.6	25	74.22	0	1.17	195/T(K)	[14]
7	1050		1312	0.6	25	74.17	0	1.67	195/T(K)	[14]
8	1159		2898	0.6	25	74.03	0	3.33	195/T(K)	[14]
9	1084	0	0	0	0	99.89	0		195/T(K)	pw
10	1012	1021	378	0	99.16	0	0	0.49	195/T(K)	[28]
11	1001	1030	880	0	99.11	0	0	1.17	195/T(K)	[28]
12	970	1075	1146	0	99.08	0	0	1.57	195/T(K)	[28]
13	898	1019	1530	0	99.65	0	0	2.27	182/T(K)	pw
14	1125	1005	281	0.6	25	74.16	0	0.33	195/T(K)	[14]
15	1177	1010	1030	0.6	25	74.10	0	1.17	195/T(K)	[14]
16	1143	992	1429	0.6	25	74.06	0	1.67	195/T(K)	[14]
17	1122	995	2805	0.6	25	73.94	0	3.33	195/T(K)	[14]
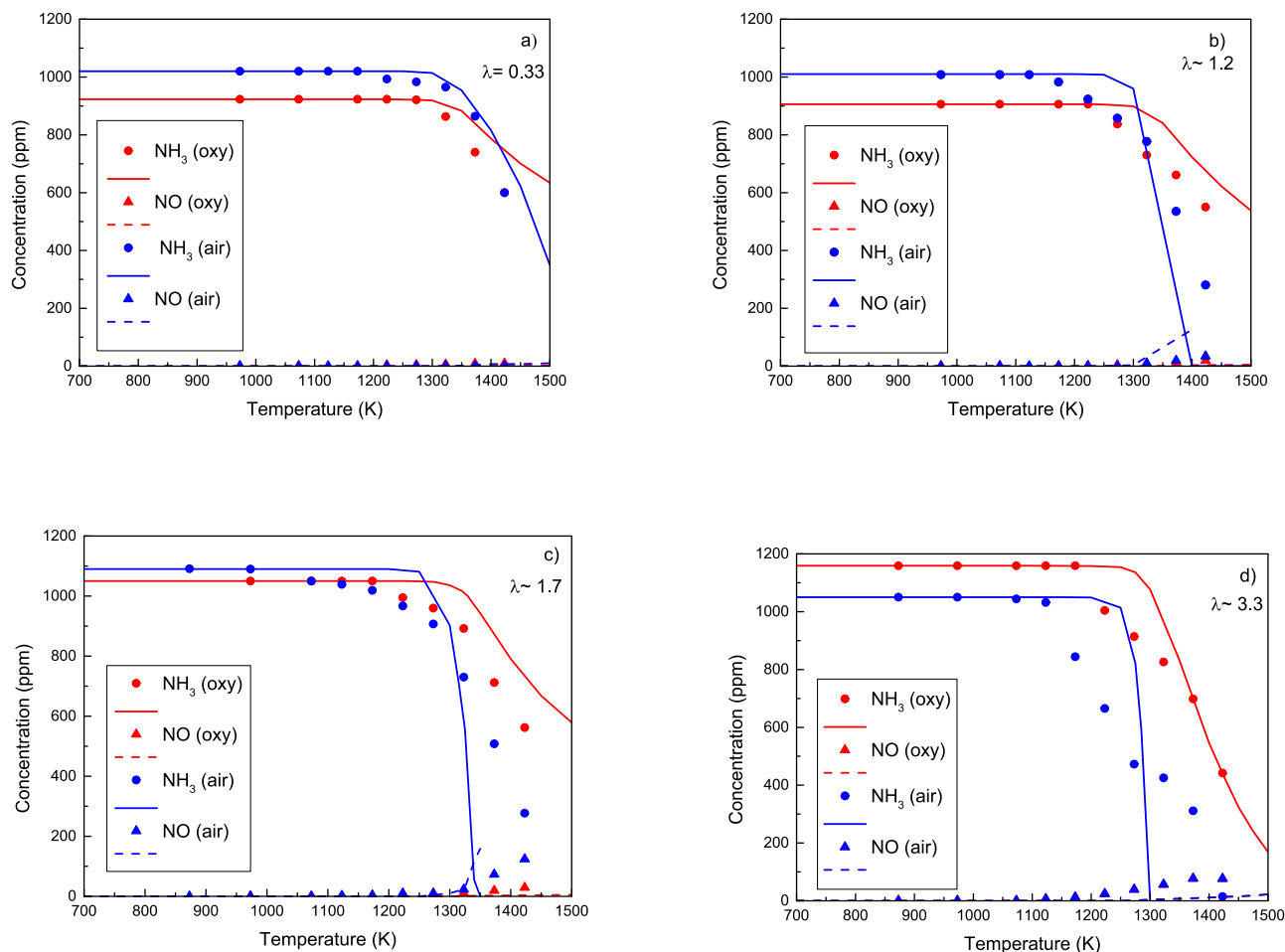
Fig. 1. NH_3 and NO concentration profiles as a function of temperature in a CO_2 or N_2 atmosphere for different stoichiometries: a) $\lambda \sim 0.3$. Sets 1 and 5 of Table 1.; b) $\lambda \sim 1.2$ Sets 2 and 6 of Table 1; c) $\lambda \sim 1.7$, Sets 3 and 7 of Table 1; d) $\lambda \sim 3.33$, Sets 4 and 8 of Table 1.

In fact, no total conversion of ammonia is detected for any of the stoichiometries considered (not even for $\lambda = 3.3$) in the CO_2 environment. Similar observations are found both experimentally and in simulations, with the NH_3 profiles in the CO_2 and N_2 atmospheres crossing at a temperature that is shifted to lower values as the stoichiometry becomes richer. This is seen for all the stoichiometries considered except for the leanest one.

This has an important relevance for practical applications·NH_3 is known for its difficulty to ignite, which is increased in the CO_2 environment. The present results, where temperature is controlled by means of the electric oven used, suggest that effects of CO_2 presence are mainly of chemical nature.

Simulations indicate that conversion of NH_3 mainly occurs by interaction with the radical pool, through (r4) to (r7) reactions, with reaction (r4) as the dominant one under any condition, and increasing the importance of (r7) as the stoichiometry is increased. As the stoichiometry is increased, the radical pool augments as well, and this is responsible for the global increase of the reaction rate.

$$NH_3 + OH \rightleftharpoons NH_2 + H_2O \quad\quad (r4)$$

$$NH_3 + H \rightleftharpoons NH_2 + H_2 \quad\quad (r5)$$

$$NH_3 + NH_2 \rightleftharpoons N_2H_3 + H_2 \quad\quad (r6)$$

$$NH_3 + O \rightleftharpoons NH_2 + OH \quad\quad (r7)$$

As the temperature increases, reaction $CO_2 \rightleftharpoons CO + O$ (r8) starts to be appreciable, increasing the presence of reactive O and OH radicals (the latter partly generated by $O + H_2O \rightleftharpoons OH + OH$ (r9), and, thus, contributing to the conversion of ammonia, by boosting (r4) and (r7) reactions. This implies a comparatively higher conversion of ammonia for $\lambda = 3.33$ compared to fuel richer stoichiometries.

Reaction (r5) is more important in the Ar/N_2 environment than with CO_2 as bath gas, where reaction (r7) is more significant than (r5). This is attributed to the fact that in the presence of CO_2, this compound also competes with NH_3 for H radicals, through:

$$CO_2 + H \rightleftharpoons CO + OH \quad\quad (r1)$$

As a result of this, conversion of NH_3 is slightly inhibited in the CO_2 scenario compared to the Ar/N_2 one.

In the presence of CO_2, reaction involving the direct interaction between NH_3 and CO_2, to produce HNCO and H_2O also occurs in a little extent:

$$NH_3 + CO_2 \rightleftharpoons HNCO + H_2O \quad\quad (r10)$$

Model calculations indicate that the HNCO formed tends to accumulate under most of the conditions considered in the present work, diminishing thus the conversion rate of NH_3 at the highest temperatures studied in the presence of CO_2. As the temperature is increased, the formed HNCO is converted back to NH_2 or NH_3 by reaction with the radical pool, mainly through:

$$HNCO + NH_2 \rightleftharpoons NCO + NH_3 \quad\quad (r11)$$

$$HNCO + H \rightleftharpoons NH_2 + CO \quad\quad (r12)$$

$$HNCO + M \rightleftharpoons CO + NH + M \quad\quad (r13)$$

Fig. 2 includes a reaction path diagram for the conversion of ammonia under the studied conditions, both in the absence and presence of CO_2. In the presence of CO_2 (red part of the figure), the path converting NH_3 into HNCO represents between 50 and 100 % for the different conditions of the present work. Later, HNCO is converted mainly into NH_2, but also into NH radicals.

In order to explore the relevance of the interaction between NH_3 and CO_2, an additional experiment (Set 9 in Table 1), in which a mixture of 1084 ppm NH_3 with CO_2 to balance was fed to the reaction system, was performed. The NH_3 and N_2 concentration results, as a function of temperature in that experiment, are represented in Fig. 3. Unfortunately, in that experiment we were not able to quantify HNCO by FTIR because of the strong signal of CO_2 in the FTIR spectrum which overlapped the HNCO profile. Fig. 3 also includes modelling calculations both with and without the (r10) reaction. As seen, since simulations with and without reaction (r10) are very similar, we can say that results are not conclusive in relation to the occurrence of a real interaction of NH_3 and CO_2 under the studied conditions. Additionally, we performed sensitivity analysis in order to find out if the results were sensitive to reaction r(r10), and results did not show any important sensitivity of the results to that reaction. An example of a sensitivity analysis for the conditions of Fig. 3 and a temperature of 1400 K is shown as Figure SM1 in the Supplementary Material.

Little formation of NO from ammonia happens, and it increases as the oxygen availability increases, but keeping as much as around 10 % or lower in any conditions studied. The model under-predicts NO formation for any stoichiometry and bath gas.

4.2. NH₃ oxidation in the presence of NO

NO can be formed during ammonia oxidation, and thus the study of the interaction of NH_3 and NO is of interest. Additionally, the impact of a high CO_2 concentration, such as that occurring in oxy-fuel combustion, may affect the interaction of the nitrogen species (NO and NH_3) compared to what happens under conventional air combustion conditions. Thus, we have studied the conversion of NH_3 in the presence of around 1000 ppm NO.

Fig. 4 (a,b,c,d) shows, for different stoichiometries ranging from fuel rich to fuel lean, the concentrations of NH_3 and NO, in the presence of NO. Fig. 5 includes the results of the concentration of O_2, where available, and the formation of N_2 in those experiments of Fig. 4 where it was

possible to measure it with precision (i.e. where Ar was used as bath gas). For all the stoichiometries studied, conversion of NH_3 occurs at a lower temperature in the Ar/N_2 atmosphere, with differences in the CO_2 atmosphere increasing as the stoichiometry becomes leaner.

There is a clearly different behavior compared to what happens in the absence of NO, Fig. 1. Thus, it is evident the important role of NO under the studied conditions. It is interesting to see that the presence of NO has a different effect if stoichiometry conditions are fuel-rich or fuel-lean. The presence of NO clearly boosts NH_3 conversion in the N_2 diluent scenario, representative of air combustion conditions. A different behavior is found in the oxy-fuel combustion environment, where the presence of NO only boosts NH_3 conversion under fuel-rich conditions, while conversion of ammonia is shifted to highest temperatures in the presence of NO as the conditions are stoichiometric or fuel-lean. The later results are of interest from a practical point of view if reduction of NO by the selective non-catalytic process (SNCR or Thermal DeNOx) is considered. In general, the presence of additives has been reported to shift the temperature window of the SNCR process to lower temperatures [e.g.,40], but the present results indicate that the presence of CO_2 has the opposite effect, and the SNCR window would be shifted to higher temperatures in the oxy-fuel combustion scenario.

In all cases, NO reacts mainly with NH_2 radicals through:

$$NO + NH_2 \rightleftharpoons N_2 + H_2O \quad\quad (r14)$$

$$NO + NH2 \rightleftharpoons NNH + OH \quad\quad (r15)$$

The increased formation of OH radicals under fuel-rich conditions, either directly in reaction (r15) or through the further evolution of NNH radicals, results in a clear promotion of NH_3 conversion by action of NO in the Ar/N_2 environment.

As mentioned, NO conversion mainly proceeds through its interaction with NH_2 radicals, but in the presence of high amounts of CO_2, NO also reacts, preferably under air excess conditions, through:

$$NO + O_2 \rightleftharpoons NO_2 + O \quad\quad (r16)$$

$$NO + HO_2 \rightleftharpoons NO_2 + OH \quad\quad (r17)$$

In the CO_2 atmosphere, CO_2 is partly converted into CO (r8) and CO further reacts in some extent with NH_2 generating HNCO (-r12). Calculations show that both CO and HNCO tend to accumulate in the reaction system, and that conversion of NH_3 is partly controlled and inhibited by the presence of those compounds, as both experiments and simulations show. As the temperature is further increased to the maximum values considered in the present work, the concentration of HNCO and CO starts to decrease, contributing to an increase of the radical pool and to the conversion of ammonia.

Conversion of NO follows the same reaction pathways independently of the CO_2 or Ar/N_2 environment, with the NH_2 + NO interaction being responsible for the final concentration of NO. Conversion of NO reaches values of around 80 % in the Ar/N_2 conditions, while no more than 50 % reduction of NO is formed in the oxy-fuel scenario for the most favorable conditions. In general, reduction of NO is limited as the stoichiometry becomes leaner, since the presence of high concentrations of O_2 favor NH_3 oxidation compared to the NH_i-NO interaction.

The presence of either Ar or CO_2 as bath gases implies a different effect on the conversion of ammonia and nitric oxide, and subsequently on the formation of N_2, which happens at significantly lower temperatures in the argon atmosphere. Actually, while conversion of NH_3 is almost complete for temperatures between 1200 and 1370 K in the Ar atmosphere, the use of an oxy-fuel environment makes the conversion of NH_3 to decrease to values lower than 20 % for the stoichiometric and slightly lean conditions. Only for the highest stoichiometry considered, $\lambda \sim 2.3, 3.3$, the conversion of ammonia is found to decrease significantly at the highest temperatures studied, reaching conversion values of around 60 %. Additionally, according to simulations, conversion of ammonia can be complete at temperatures around 1500 K. The fact that
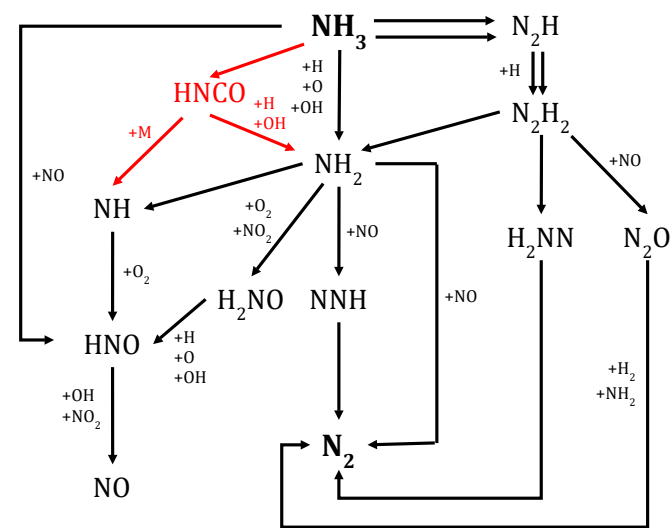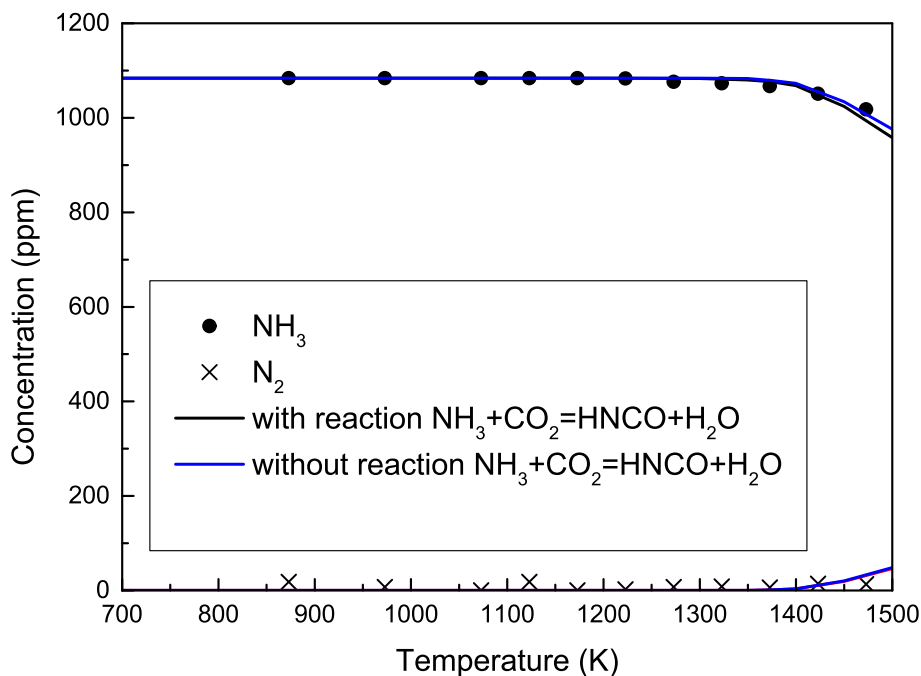

Fig. 2. Reaction path diagram for the conversion of ammonia under the conditions of the present work. Black lines correspond to pathways occurring in both N_2/Ar and CO_2 environments, while red lines correspond to reactions occurring only in the CO_2 diluted scenario.

Fig. 3. NH_3 and N_2 concentration profiles as a function of temperature as a result of the interaction between NH_3 and CO_2 in a CO_2 atmosphere Set 9 of Table 1.
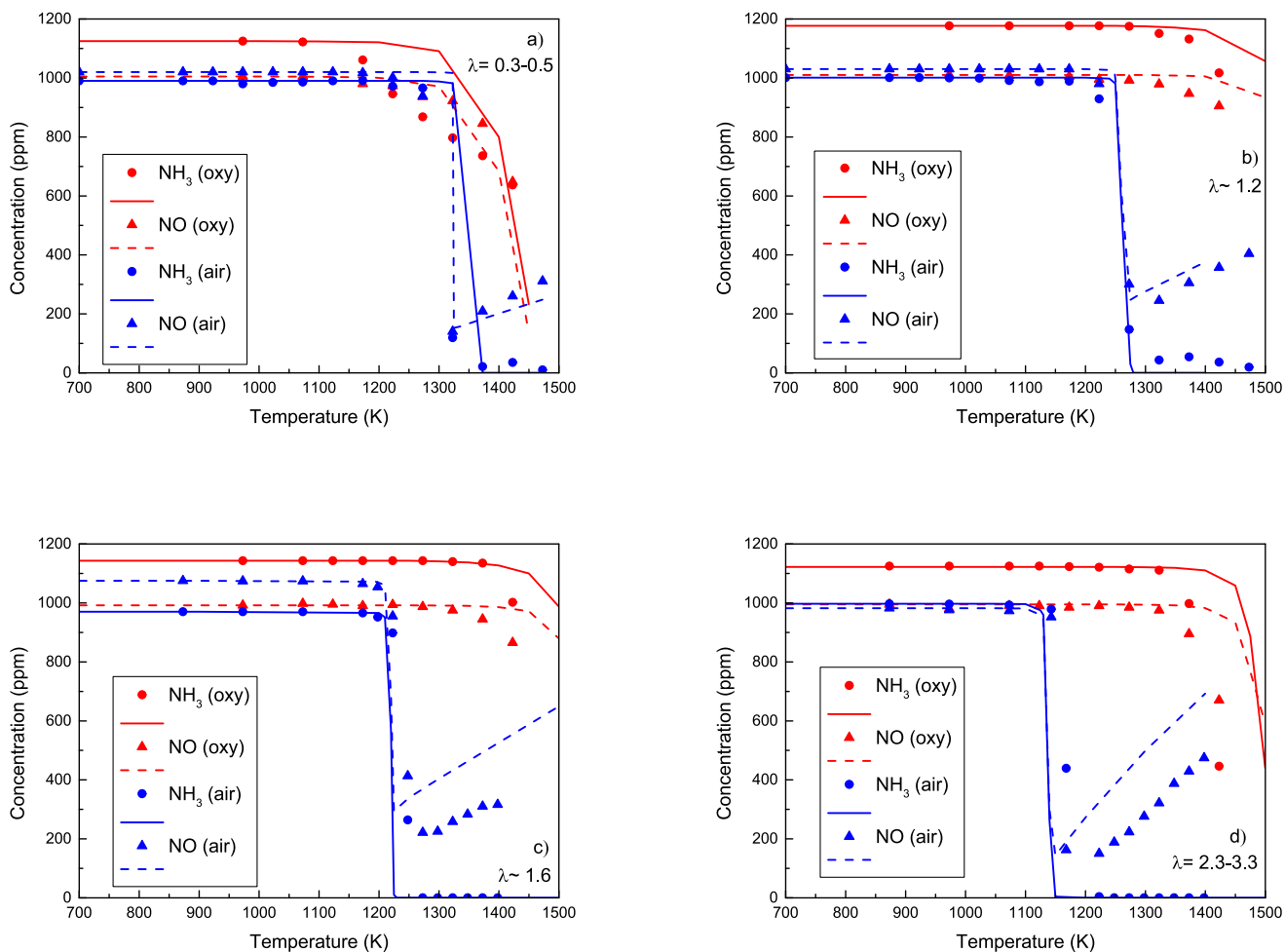

Fig. 4. NH_3 and NO concentration profiles, in the presence of around 1000 ppm NO, as a function of temperature in an oxy-fuel (CO_2) or air (N_2 or Ar) atmosphere for different stoichiometries: a) $\lambda \sim 0.3, 0.5$. Sets 14 and 10 of Table 1; b) $\lambda \sim 1.2$ Sets 11 and 15 of Table 1; c) $\lambda \sim 1.6$ Sets 12 and 16; d) $\lambda \sim 2.3, 3.3$, Sets 13 and 17.
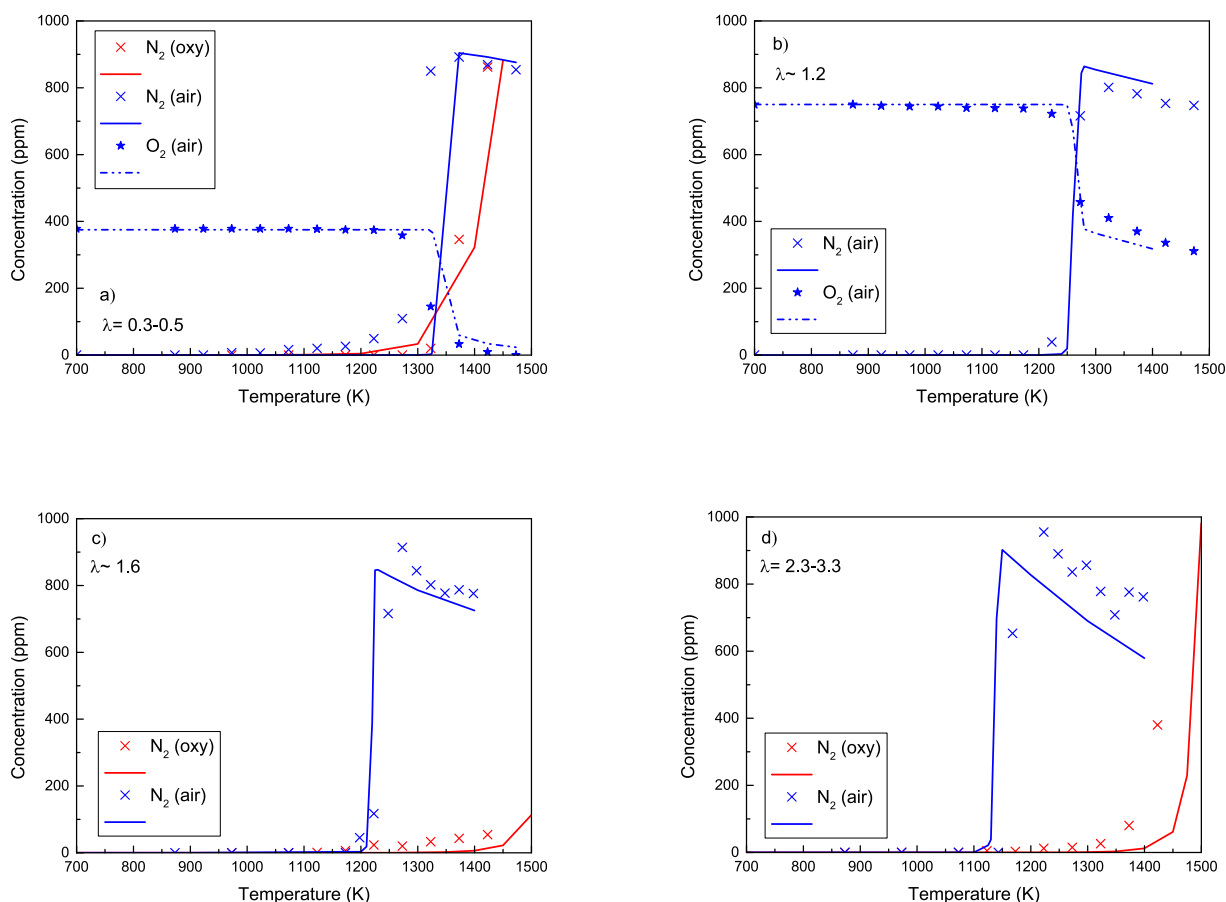
Fig. 5. N_2 and O_2 concentration profiles, in the presence of around 1000 ppm NO, as a function of temperature in an oxy-fuel (CO_2) or air (N_2 or Ar) atmosphere for different stoichiometries: a) $\lambda \sim 0.3, 0.5$. Sets 14 and 10 of Table 1; b) $\lambda \sim 1.2$ Sets 11 and 15 of Table 1; c) $\lambda \sim 1.6$ Sets 12 and 16; d) $\lambda \sim 2.3, 3.3$, Sets 13 and 17.

conversion of ammonia occurs at significantly higher temperatures in the oxy-fuel combustion conditions compared to those representative of air combustion may be a drawback for the use of oxy-fuel technologies with ammonia, as well as for mixing ammonia with biofuels as biogas.

Fig. 5 (a,b,c,d) shows the results of the N_2 formed in either the oxy-fuel and Ar/N_2 combustion conditions, for the same experiments as in Fig. 4. Results indicate that a significant fraction of the nitrogen entering to the reactor is converted to molecular nitrogen. The simulated N_2 profiles agree reasonably well with the experimental determinations, and disagreements observed for the leanest conditions considered coincide with disagreements in NO concentration, while the nitrogen balance is well described by the model. Also, the profile of O_2 concentration shown in Fig. 5a is pretty similar in both experimental and simulated data, indicating the goodness of the model used for calculations.

5. Conclusions

The impact of using either oxy-fuel or air combustion conditions on the conversion of NH_3 is analyzed from experimental and simulation study points of view. The study has been performed at atmospheric pressure under carefully controlled conditions, varying important variables such as temperature and stoichiometry. Also, the impact of the presence and concentration of NO has been evaluated in both the CO_2 or the Ar/N_2 scenarios, representative respectively of oxy-fuel and air combustion conditions. The experimental results have been interpreted with an updated literature detailed chemical-kinetic mechanism.

The results obtained indicate that the CO_2 environment, compared to the O_2/N_2 or Ar one, implies a slight inhibition of ammonia conversion, in particular at high temperatures. The inhibition of NH_3 conversion by

CO_2 is attributed to the competence for hydrogen radicals between NH_3 and CO_2.

No significant direct interaction of ammonia and CO_2 has been found for the low concentrations of reactants used in the present experiments. Calculations indicate that HCNO is formed as intermediate product, especially in the intermediate temperatures considered, but it hasn't been possible to identify it experimentally.

The presence of NO, which can be formed as well from NH_3 oxidation, has an important effect on the conversion regime of NH_3. NO strongly inhibits the conversion of ammonia in the oxy-fuel atmosphere compared to the N_2-Ar environment under fuel lean conditions, while it boosts NH_3 conversion under fuel rich conditions. As a result of this, reduction of ammonia is much higher in the Ar/N_2 environment compared to the oxy-fuel conditions in the temperature range studied.

The detailed kinetic mechanism, taken from the literature and used in calculations, is able to reproduce the main trends observed experimentally, as well as the ammonia and products concentration profiles.

The present results are of interest for practical industrial applications, and they indicate a certain drawback for ammonia to be burned in oxy-fuel combustion conditions or mixed with CO_2 containing biofuels.

CRediT authorship contribution statement

María U. Alzueta: Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Formal analysis, Conceptualization. **Víctor D. Mercader:** Methodology. **Jorge Giménez-López:** Methodology. **Rafael Bilbao:** Writing – review & editing, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2023.129212.

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