



Full Length Article

Conversion of NH₃ and NH₃-NO mixtures in a CO₂ atmosphere. A parametric study

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ABSTRACT

The present work addresses the oxidation of ammonia and ammonia-nitric oxide mixtures in a CO₂ atmosphere, characteristic of oxy-fuel processes and/or biogas combustion, from both experimental and kinetic modelling points of view. A parametric study of NH₃ and NH₃/NO mixtures oxidation is carried out, evaluating the influence of the temperature (700–1500 K), stoichiometry (from pyrolysis, $\lambda = 0$, to significantly oxidizing conditions, $\lambda = 3.3$), gas residence time (low values, 195/T(K) s and high values, 3100/T(K) s) and NH₃/NO ratio (0.5–2.2), at atmospheric pressure under well-controlled laboratory conditions using two tubular flow reactor setups. Experimental results have been simulated with an updated literature reaction mechanism, which has been used to interpret the experimental observations.

1. Introduction

The problems derived from CO₂ emissions are very well known. Different strategies have been proposed to minimize these emissions, such as the use of biofuels or carbon free fuels. Among the latter ones, ammonia is believed to be a competitive candidate [1]. NH₃ exhibits a relatively high energy density and a low vapor pressure, which facilitates the transport and storage compared to the use of H₂ [2]. In order to facilitate combustion and even the transition to a pure NH₃ economy, ammonia may also be mixed with other fuels, such as H₂ and/or CH₄ [3–5].

An interesting possibility is the use of NH₃-biofuel mixtures, being biogas an appropriate biofuel. Biogas consists mainly of CH₄ and CO₂, and the presence of CH₄ decreases the temperature of NH₃ ignition. Logically, the combustion of biogas also produces CO₂ in the exhaust gas, although because biogas is considered as biofuel, neutral emissions of CO₂ can be assumed. Another additional solution to reduce CO₂ emission is oxy-fuel combustion. This process uses oxygen instead of air in order to significantly increase the CO₂ concentration of the exhaust gas, due to the absence of N₂, and this is beneficial for carbon capture strategies. It is true that ammonia combustion will produce N₂, although CO₂ concentration would still be high. Therefore, biogas combustion and/or the use of oxy-fuel combustion causes the process to occur in an overall CO₂ atmosphere.

The main drawback of using ammonia is related to the possible

formation of nitrogen oxides. This fact is of particular importance in oxy-fuel combustion scenarios where the only source of NO is the oxidation of ammonia. It is worthwhile to note that the joint presence of NH₃ and NO in a fuel-lean atmosphere is representative of conditions occurring during the selective non catalytic reduction of NO, process which is extensively used as a NO_x reduction technology [e.g. 6]. In this sense, NO may be minimized in-situ during the ammonia combustion process. There are a number of studies in the literature addressing the conversion of ammonia [e.g. 7, 8] and the interaction of ammonia and nitric oxide [9–13], but most of them are carried out in air combustion conditions. Results indicate that the conversion of ammonia can produce both molecular nitrogen or nitric oxide, in different amounts depending on the specific operating conditions, and that the interaction of NH₃ and NO does occur, leading to very low NO emissions if the selected operating conditions are adequate [7–13]. Few studies have addressed the conversion of ammonia in the presence of significant amounts of CO₂. In particular, the works of Mendiara and Glarborg [14,15] address the conversion of ammonia and the reduction of NO by methane-ammonia mixtures under oxy-fuel combustion conditions in a combined experimental and kinetic modelling study. They observed that using CH₄, the reduction of NO attained was similar in N₂ and CO₂ under reducing conditions, but increased in a CO₂ atmosphere for stoichiometric and lean conditions, compared to the conventional air environment. The conversion of ammonia and the formation of NO in a CO₂ atmosphere have also been recently studied by Ding et al. [16] and Li et al. [17] in a

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jet-stirred reactor. The authors performed both experimental and simulation works and brought interesting conclusions related to the conversion regime of ammonia in a high CO₂ concentration environment. Other works related to oxy-fuel combustion include the analysis of the effect of CO₂ [18] or steam [19] for the conversion of ammonia to NO, or determinations of laminar speed flames [4], as well as the use of different combustion technologies as cyclone combustors [20].

In an oxy-fuel combustion scenario, the recirculation of the flue gas may cause an accumulation of pollutants, nitrogen oxides in particular or the unreacted ammonia if any. The high CO₂ levels that may be present if biogas-ammonia mixtures are burned would not be expected to directly affect significantly the interaction between NH₃ and NO. However, high concentrations of CO₂ are known to affect the O/H/OH radical pool, through the CO₂ + H = CO + OH reaction [21], and thus may affect the combustion chemistry of NH₃ and NH₃-NO mixtures.

In this context, the present work aims to study the oxidation of NH₃ and the interaction of NH₃ and NO in a CO₂ atmosphere, characteristic of biogas or oxy-fuel combustion processes. The study is carried out from both experimental and kinetic modeling points of view using tubular flow reactor experimental installations and a literature detailed kinetic mechanism.

2. Experimental methodology

Experiments have been carried out in two different experimental installations (A and B), both consisting basically of a gas feeding system, a reaction system, and a gas analysis system. Gas feeding and analysis is common to both reaction systems. These systems allow us to perform experiments for very different gas residence times and temperature ranges.

Reaction system A includes a quartz flow reactor with a reaction zone of 8.7 mm internal diameter and 200 mm in length, which is placed in a three-zone electrically heated oven, which ensures an isothermal temperature throughout the reaction zone within ± 10 K. Detailed description of this system can be found in Alzueta et al. [22]. The temperature in the reaction zone was measured with a type-K fine-wire thermocouple. Gases (N50) are led to the reactor from cylinders through mass flow controllers by four separate injectors, a main stream and three additional side streams. The main stream containing O₂ diluted in CO₂ is preheated in the reactor and mixed with the other feed gases (NH₃, NO, and Ar) at the inlet of the reaction zone. An additional experiment in a N₂ atmosphere was also performed in order to compare the results with CO₂ and N₂ as bath gases. A total gas flow rate of 1000 mL (STP)/min is kept constant during the experiments, leading to a gas residence time, in the reaction zone, as a function of the reaction temperature, t_r (s) = 195/T [K]. The mixture is highly diluted, low heat is released during the reaction and therefore no influence of the reaction on the temperatures can be assumed. At the outlet of the reaction zone, the product gas is cooled by means of external refrigeration with air and conducted to the analysis system.

Reaction system B includes a non-porous alumina tube reactor with 40 mm internal diameter and 800 mm in length. The reactor is placed in an electrically heated oven which allows temperatures up to 1800 K. The longitudinal temperature profile in the reactor was measured with a type-S platinum ceramic-covered thermocouple placed inside the reactor and results in an almost isothermal temperature (within ± 20 K) which is attained throughout the main reaction zone of 150 mm approximately, with steep temperature gradients toward both the inlet and outlet of the reaction zone. Gases are led to the reactor from cylinders through mass flow controllers and all reactants are premixed before entering the reactor. A total gas flow rate of 1000 mL (STP)/min is kept constant during the experiments, leading to a gas residence time as a function of the reaction temperature, t_r (s) = 3100/T [K]. A full description of the reaction system and experimental procedure can be found for example in Giménez-López et al. [23].

A gas chromatograph equipped with TCD and FID detectors is used to

measure CO, CO₂, N₂ and H₂. NO concentration is measured by means of a continuous IR analyzer. The gas stream is also analyzed by a Fourier Transform Infrared (FTIR) spectrometer, where NH₃, N₂O and NO₂ are measured. The uncertainty of the measurements is estimated as $\pm 5\%$, except for the values of the compounds detected with the FTIR spectrometer, which is $\pm 10\%$. In all the experiments, very low, negligible, concentrations of N₂O and NO₂ are detected, and consequently are not shown.

Table 1 shows the conditions of the different experiments.

With the exception of experiment 1, that has been performed in a N₂ atmosphere, representative of conventional combustion conditions, the rest of experiments (2 to 17) have been made in a CO₂ atmosphere, representative of oxy-fuel combustion conditions. The CO₂ concentration values around 75 % have been taken as representative of the oxy-fuel combustion atmosphere according to the work of Giménez-López et al. [21]. Most of experiments contain water, for two reasons. On the one hand, water is a product of the combustion reaction of ammonia and will be present as a reaction product. On the other hand, the presence of water assures a high concentration of the O/H radical pool and thus will minimize, if any, potential surface effects, by minimizing the effect of radical recombination in the reactor walls. In the experiments in the presence of CO₂, Ar is used to balance the flow rate up to 1000 mL/min (STP). Comparison of experiment 1, with N₂ as bath gas, and experiment 4 with CO₂ as bath gas allows us to compare the results obtained under the two reaction atmospheres for similar operating conditions.

While most of the experiments have been made in installation A with a gas residence time of 195/T(K) seconds, sets 1 to 12 in Table 1, certain experiments, sets 13 to 17, in the presence of NO have been performed with a higher residence time of 3100/T(K) seconds, in installation B.

The stoichiometry (λ) is defined as the quotient between the oxygen/fuel relation available for reaction and the stoichiometric oxygen/fuel relation, in the following reaction:



The influence of λ (0.33, 1.17, 1.67 and 3.33) on NH₃ oxidation in the CO₂ atmosphere has been studied in installation A for a given residence time, experiments 3 to 6 in Table 1. Also, influence of λ has been faced by means of a pyrolysis experiment, i.e. $\lambda = 0$, experiment 2 in Table 1.

The impact of NO presence on NH₃ conversion and the reduction of NO that can be attained have been considered by adding approximately 1000 ppm NO (experiments 7 to 10). Also, the influence of NO concentration has been studied for a given λ value, $\lambda = 1.67$ (experiments 9, 11 and 12 for the residence time of 195/T(K) s in installation A, and 14, 16, and 17 for the residence time of 3100/T(K) s in installation B), resulting in different NH₃/NO ratios, between approximately 0.5 and 2.

3. Kinetic modelling

Model calculations have been performed using the PFR model of the Chemkin Pro suite [24]. The mechanism used for simulations is largely based on the model of Glarborg et al. [25], with minor updates and extended to include CH₃CN conversion [26]. This reaction mechanism includes submechanisms for C1-C2 hydrocarbons [27–29], amines [30] cyanides [31] and hydrocarbon/nitrogen interactions [14,15,32], and the interaction of NH₃ and NH₂ to produce N₂H₃ and H₂, which was found to be important to describe NH₃ oxidation in an air atmosphere [8], as described in the work of Dove and Nip [33].

Under oxy-fuel combustion conditions, the concentration levels of CO₂ are comparatively high. Thermal decomposition of CO₂ is highly endothermic and is relevant only at high temperatures,



Reactions of CO₂ with the radical pool can occur at comparatively lower temperatures. The main reaction of CO₂ with radicals is its interaction with H radicals, which is important even at moderate

Table 1

Experimental conditions.

Set	NH ₃ (ppm)	NO (ppm)	O ₂ (ppm)	H ₂ O (%)	Ar (%)	CO ₂ (%)	N ₂ (%)	λ	t _r (s)
1	1008	0	882	0.6	0	0	99.21	1.17	195/T(K)
2	1040	0	0	0	24.9	75	0	0	195/T(K)
3	923	0	231	0.6	25	74.28	0	0.33	195/T(K)
4	906	0	793	0.6	25	74.22	0	1.17	195/T(K)
5	1050	0	1312	0.6	25	74.17	0	1.67	195/T(K)
6	1159	0	2898	0.6	25	74.03	0	3.33	195/T(K)
7	1125	1005	281	0.6	25	74.16	0	0.33	195/T(K)
8	1177	1010	1030	0.6	25	74.10	0	1.17	195/T(K)
9	1143	992	1429	0.6	25	74.06	0	1.67	195/T(K)
10	1122	995	2805	0.6	25	73.94	0	3.33	195/T(K)
11	1131	505	1414	0.6	25	74.11	0	1.67	195/T(K)
12	1090	1975	1363	0.6	25	73.97	0	1.67	195/T(K)
13	1008	1029	875	0.6	25	74.11	0	1.17	3100/T(K)
14	1022	1029	1277	0.6	25	74.07	0	1.67	3100/T(K)
15	1033	1015	2582	0.6	25	73.95	0	3.33	3100/T(K)
16	1048	502	1312	0.6	25	74.08	0	1.67	3100/T(K)
17	1010	2005	1262	0.6	25	74.03	0	1.67	3100/T(K)

temperatures, and is responsible for the partial equilibrium between CO and CO₂ under combustion conditions,



This reaction has been extensively studied and it is well-known in a large temperature and pressure interval (see for instance the revision of Rasmussen et al. [34]). For this reaction, the value recommended by Baulch and Drysdale [35] has been used, which roughly agrees with the later determinations for the kinetic constant of this reaction.

Reactions of CO₂ with other radicals, such as O and OH, reactions 4 and 5, are too slow to be relevant under the studied conditions:



CO₂ is able to interact with some reactive radicals of the N/O/H system. The CO₂ + N reaction has been reported to contribute to NO formation under fuel-rich conditions, in CH₄ flames with various O₂ concentrations [36]. The first studies of the kinetic parameters for the CO₂ + N ⇌ CO + NO (r6) reaction were those of Avramenko and Krasnen'kov [37] who obtained an experimental determination in a vacuum system, assuming that the reaction was relatively fast. Later, Herron and Huie [38] performed a mass spectrometric study of that reaction in the 298–523 K temperature range, and later Fernández et al. [39] studied that reaction in a high temperature photochemical reactor. The two latter works indicated that the reaction was slow and little important under combustion conditions. This was confirmed by the theoretical study of Manaa and Chabalowsky [40] who obtained a high energy barrier for this reaction. The present work uses the rate constant proposed by Glarborg et al. [6] which agrees well with the upper limit proposed by Fernández et al. [39] and with the shock wave measurements of Lindackers et al. [41].

Röhrig and Wagner [42] determined the rate constants of the CO₂ + NH interaction (reaction r7) from incident shock wave experiments, finding that the reaction was significantly fast and that the only products thermodynamically stable for that reaction (r7) were HNO + CO in the studied temperature range of 1200–1900 K.



Later, Fontijn et al. [43] disregarded those species as reaction products, based on their theoretical studies which indicate much higher activation energies compared to the determinations of Röhrig and Wagner [42]. Fontijn et al. [43] proposed the formation of reaction adducts able to react, but they were not finally able to specify the products of that reaction. Similar conclusions were reached by Mackie and Backsaj [44], who concluded that the formation of HNO + CO as

products was only significant above 1500 K. Since uncertainty in relation to this reaction is high, we have chosen HNO + CO as the only product channel for the CO₂ + NH reaction, using the kinetic parameters of Mackie and Backsaj [44] for the global reaction, which are significantly lower than those proposed by Röhrig and Wagner [42]. While this reaction has not been to be particularly relevant under the conditions of the present work, it exhibits a high uncertainty and would deserve a proper determination.

An experimental shock wave study by Wooldridge et al. [45] allowed to detect the formation of CO₂ + NH₂ as a minority product channel of the HNCO + OH interaction. The authors established a maximum contribution of 10 % for that reaction channel in the 1250–1860 K temperature range. This low value for the reaction constant is consistent with other studies [46,47], which suggest NCO and H₂O as majority products, reactions:



In the present work, the channel producing CO₂ is kept, despite its expected low contribution in the high CO₂ atmosphere.

The reaction of CO₂ with NO may affect the NO/NO₂ equilibrium. The study for the direct interaction by Clark et al. [48] establishes an upper limit for the constant of this reaction of 3.01*10⁹ cm³/mol s. On the contrary, the reverse reaction has been more studied. In the present work, we use the theoretical determination by Kroupnov and Pogosbekian [49], for this reverse step, reaction r10, which agrees roughly with other literature determinations [50–52].



In the high CO₂ concentration environment, the interaction between NH₃ and CO₂ may potentially be important, and is included in the mechanism, reaction:



Cheng et al. [53] used density functional theory (DFT) calculations to investigate the synthesis mechanism of cyanuric acid from NH₃ + CO₂ and provided the mechanism for reaction and energy barriers involved, indicating that those are relatively high. Later, Glarborg et al. [25] included the reaction of HNCO + H₂O as a possible reaction for HNCO conversion during the oxidation of this compound, indicating that the interaction of HNCO with water would result in NH₃ + CO₂. Under the conditions of the present work, and because of the high concentrations of CO₂, this reaction is seen play a role, as is later discussed.

The full mechanism is included in Chemkin format in the supplementary material.

4. Results and discussion

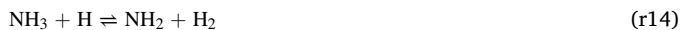
The influence of N_2 and CO_2 atmospheres can be seen in Fig. 1, where comparison of experimental results carried out in similar conditions with and without CO_2 and roughly stoichiometric conditions is seen. The conversion of ammonia in the air atmosphere seems to start at slightly lower temperatures compared to the CO_2 environment, and the presence of high amounts of CO_2 seems to slow down ammonia conversion even more at the highest temperatures studied in the present work. The model is able to catch this feature, even though the specific values of concentrations are not well matched. Calculations indicate that the reason for the different behavior obtained in the presence of CO_2 is attributed to the main reactions consuming NH_3 in each case.

In the presence of CO_2 , NH_3 reacts with OH and NH_2 radicals and with CO_2 , through reactions r11 to r13:



In the CO_2 environment, and at the temperature of 1350 K, reaction r12 implies a 48 % of NH_3 conversion, followed by r13 (25 %) and r11 proceeding in the reverse sense, i.e. -r11, (23 %). Similar reactions dominate the high temperature conversion of NH_3 at high temperatures in the same atmosphere, even though the contribution of the reactions is different. It is thus seen that a direct interaction of ammonia and carbon dioxide occurs under the studied experimental conditions.

In the air (O_2/N_2) environment, NH_3 reacts with different components of the radical pool (OH, NH_2 , H and O radicals) and logically the interaction with CO_2 can not occur. In this case, NH_3 is converted through reactions r12 and r13, and r14 and r15 at the onset of conversion, i.e. ca 1300 K:



but, as the temperature increases, only interaction with NH_3 with the O/H radical pool happens, with negligible reaction with NH_2 radicals (r13).

The influence of stoichiometry on ammonia oxidation in a CO_2 atmosphere, representative of oxy-fuel combustion conditions, is shown in Fig. 2, and the formation of NO and N_2 are shown in Figs. 3 and 4 respectively. Conditions represented range from pyrolysis ($\lambda = 0$) to significantly fuel lean ones ($\lambda = 3.33$), sets 2–6 in Table 1. In agreement

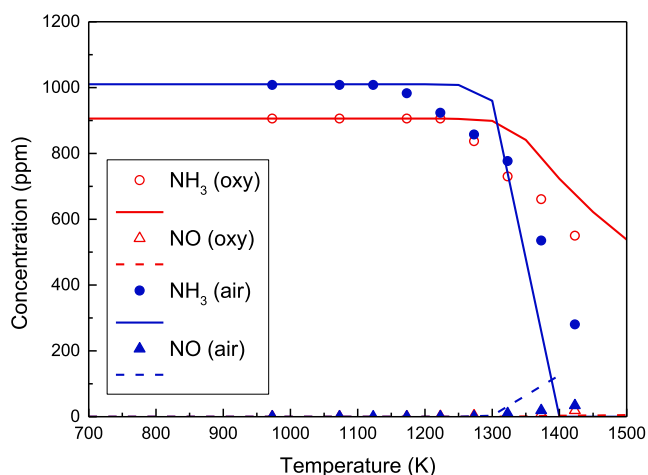


Fig. 1. NH_3 and NO concentration profiles as a function of temperature, for a stoichiometry of $\lambda = 1.17$ in either a N_2 /air (Set 1 in Table 1) or an oxy/ CO_2 atmosphere (Set 4 in Table 1).

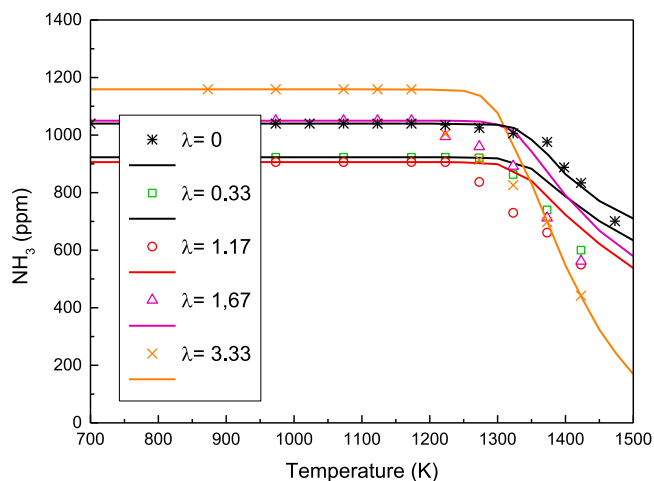


Fig. 2. NH_3 concentration profiles as a function of temperature, for different stoichiometries in an oxy/ CO_2 atmosphere (Sets 2–6 in Table 1).

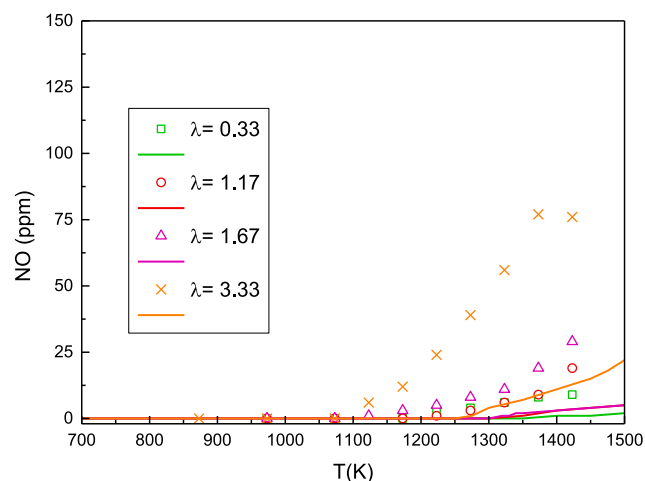


Fig. 3. NO concentration profiles as a function of temperature, for different stoichiometries in an oxy/ CO_2 atmosphere (Sets 2–6 in Table 1).

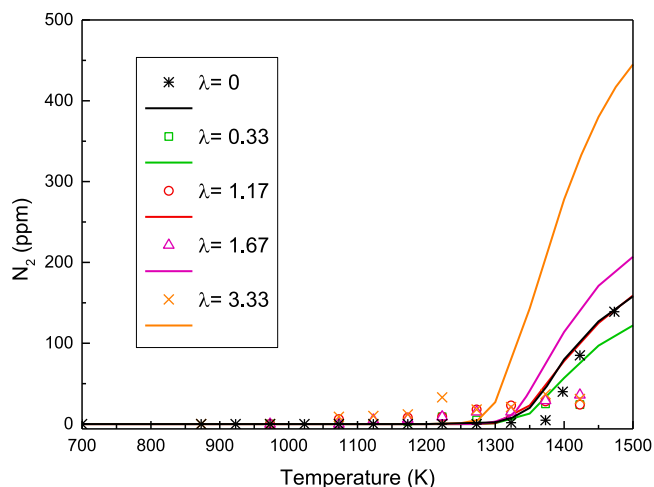


Fig. 4. N_2 concentration profiles as a function of temperature, for different stoichiometries in an oxy/ CO_2 atmosphere (Sets 2–6 in Table 1).

with the known effect of a high availability of oxygen promoting conversion of ammonia [e.g. 8], the higher radical pool reserve at lean conditions is responsible for a higher conversion of NH_3 at a given temperature. However, differences in the conversion profiles of NH_3 , as a function of temperature for the different stoichiometries studied, are not very important, with maybe the exception of $\lambda = 3.33$, where the availability of O/H free radicals is considerably higher. The higher conversion of NH_3 occurring with the increase in O_2 concentration is accompanied by a higher formation of NO, despite the low values of this compound attained for all the temperature range considered, except for the most oxidizing conditions studied, where the higher NH_3 consumption facilitates a higher formation of NO.

The experimental nitrogen atoms balance, calculated as the sum of nitrogen in NH_3 , NO and N_2 closes very well until a temperature of approximately 1300 K. Above this temperature, deviations in the balance occur, which seems to indicate that other species than those mentioned appear in the reaction system. Model calculations above this temperature indicate the formation of a high number of different nitrogen species in small concentrations, which may be the reason of the unbalanced nitrogen.

While the model used in simulations reproduces fairly well the NH_3 concentration profiles, the formation of NO is underestimated. However, as it has been mentioned above, the amount of NO formed is low, below 40 ppm under the conditions studied, except for the leanest case in which NO reaches approximately 80 ppm. On the contrary, the formation of N_2 is overestimated by the model, even though again the measured experimental concentrations are low, with maximum values measured of around 100 ppm. Anyway, while the main trends are fairly well reproduced by the model, it seems that it is not fully able to predict properly the conversion of NH_3 into N_2 or NO. At present, we do not know the specific reason for such issue, but it may be related to the conversion of the intermediate species in the presence of the high concentrations of CO_2 .

Figs. 5 to 7 show the impact of the presence of approximately 1000 ppm NO on the conversion of around 1000 ppm NH_3 as a function of temperature for different stoichiometries. Results indicate that the presence of NO has different effects depending on the stoichiometry. Under fuel rich conditions, NO acts to promote NH_3 oxidation. However, for stoichiometric and fuel-lean conditions, the presence of NO inhibits the conversion of NH_3 at the temperatures of its initiation. This happens because of a complex mechanism involving the radical pool concentration and speciation and the competition of NO for NH_2 radicals and other species, in the experiments in the presence of NO.

As mentioned before, in the absence of NO, conversion of NH_3

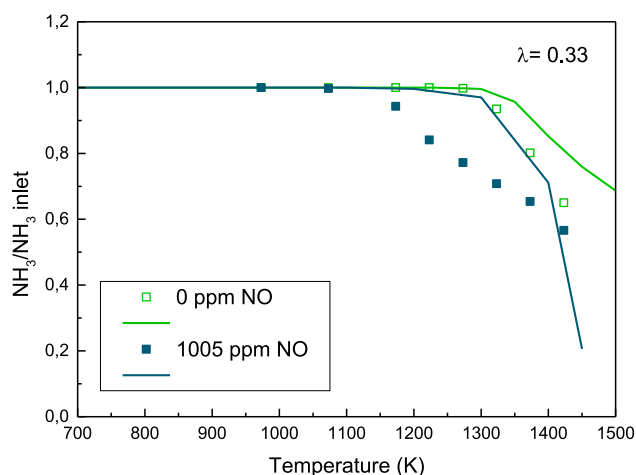


Fig. 5. Normalized NH_3 concentration (NH_3/NH_3 inlet) as a function of temperature, in the absence and presence of NO for a stoichiometry of $\lambda = 0.33$ (Sets 3 and 7 in Table 1).

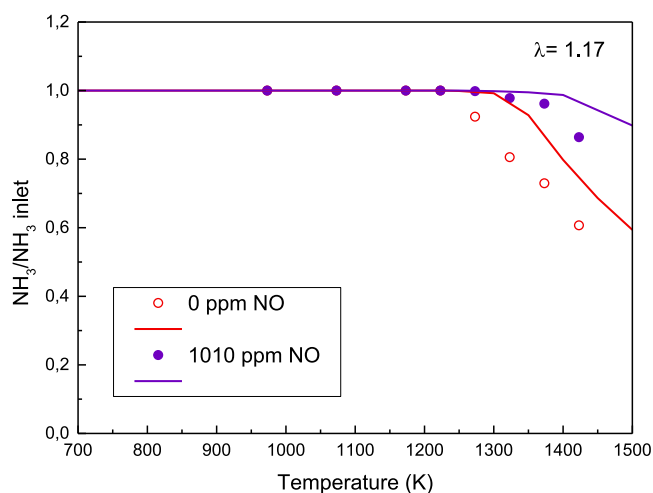


Fig. 6. Normalized NH_3 concentration (NH_3/NH_3 inlet) as a function of temperature, in the absence and presence of NO for a stoichiometry of $\lambda = 1.17$ (Sets 4 and 8 in Table 1).

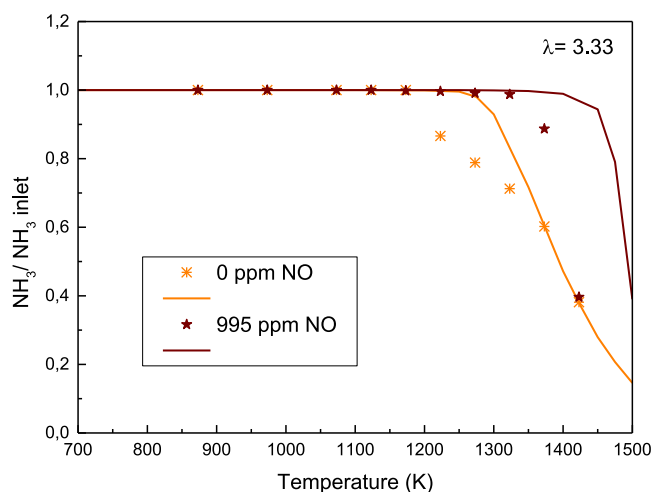


Fig. 7. Normalized NH_3 concentration (NH_3/NH_3 inlet) as a function of temperature, in the absence and presence of NO for a stoichiometry of $\lambda = 3.33$ (Sets 6 and 10 in Table 1).

mainly proceeds through reactions r11 to r15. While in the absence of NO, conversion of NH_3 is shifted to lower temperatures as the stoichiometry becomes more oxidant, which is attributed to the higher availability of radicals because of the radical building up with temperature, in the presence of NO a different behavior is observed.

When NO is present, reaction r13 ($\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$) is not active since NO competes with NH_3 for NH_2 radicals and in fact NO dominates the consumption of NH_2 radicals which are present in high levels through reactions r16 and r17, mainly for high oxygen concentrations. Under reducing conditions, the amount of NH_2 radicals is comparatively limited and NO reacts through reactions r16 to r19:



leading to an increase of radicals, mainly OH that, in turn, favors conversion of NH_3 into NH_2 radicals. Figure SM1 in the supplementary material summarizes the reactions happening during the conversion of

ammonia under the conditions of the present work in the form of a reaction pathway diagram.

In order to analyze the full temperature range where ammonia conversion occurs, experiments in a different setup with a ceramic reactor were performed, sets 13 to 17 of Table 1. Figs. 8 and 9 show respectively the results of NH_3 and NO for different stoichiometries and as a function of temperature obtained with a significantly higher gas residence time. As seen, model calculations (lines) reproduce the main experimental trends (as symbols) even though are shifted about 40 K to higher temperatures. It is seen both experimentally and by model calculations that the conversion at $\lambda = 1.17$ and 1.67 occurs at a approximately the same temperatures, while increasing O_2 availability up to $\lambda = 3.33$ shifts conversion to comparatively lower temperatures. The increase in residence time to $3100/T(\text{K})$ of Figs. 8 and 9 compared to the value of $195/T(\text{K})$ of earlier representations (e.g. Figs. 5-7, solid symbols) acts to shift the conversion regime of ammonia more than 100 K, which indicates the importance of this parameter and its influence on the building up of the radical pool under the studied conditions.

Figs. 10–13 show the impact of varying the amount of NO keeping constant the inlet NH_3 concentration, i.e. varying the the NH_3/NO ratio, on the concentrations of NH_3 and NO for two different residence times, one approximately 16 times higher compared to the other. The results obtained with the low residence time ($195/T(\text{K})$) are shown in Figs. 10 and 11 and those corresponding to the high residence time ($3100/T(\text{K})$) in Figs. 12 and 13.

For the low residence times considered, results indicate that the effect of varying the NH_3/NO ratio is negligible on both the NH_3 and NO concentrations, while for the high residence time studied, the different NO concentrations do have a slight effect on the conversion regime of NH_3 and NO. Compared to the NH_3/NO ratio of approximately 1, increasing the NH_3/NO ratio (i.e. decreasing NO concentration) shifts NO conversion to lower temperatures, while NH_3 conversion is slightly shifted to higher temperatures. As NO concentration increases, reaction $\text{NH}_3 + \text{OH} \rightleftharpoons \text{NH}_2 + \text{H}_2\text{O}$ is comparatively more important compared to the $\text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{HNCO} + \text{H}_2\text{O}$ reaction, which implies a comparatively high concentration of NH_2 radicals. Thus, under these conditions the extent of the $\text{NH}_2 + \text{NO}$ reaction is increased and the chain branching step where NH_2 is implicated is activated. This effect is more important for high residence times.

5. Conclusions

An experimental and simulation study of the oxidation of ammonia in a CO_2 atmosphere, representative of biogas or oxy-fuel combustion has been performed in a variety of experimental conditions. The study

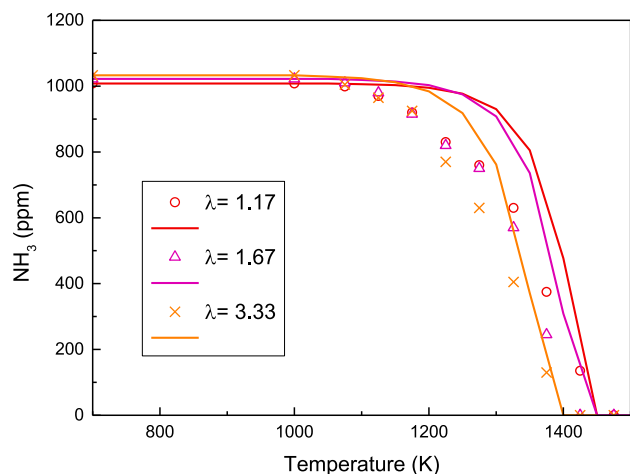


Fig. 8. NH_3 concentration as a function of temperature for different stoichiometries and a high residence time (Sets 13 to 15 in Table 1).

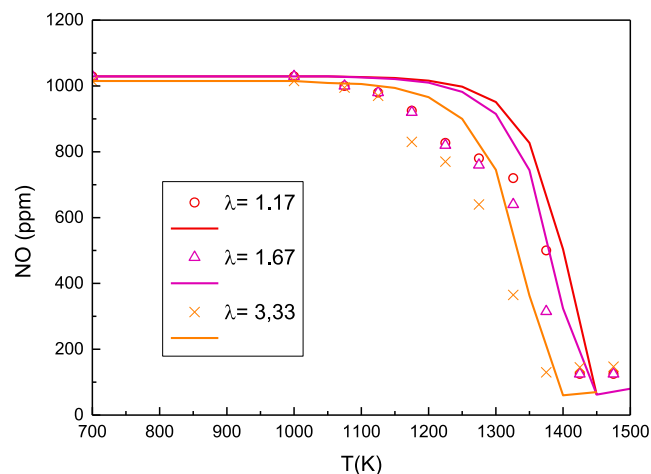


Fig. 9. NO concentration as a function of temperature for different stoichiometries and a high residence time (Sets 13 to 15 in Table 1).

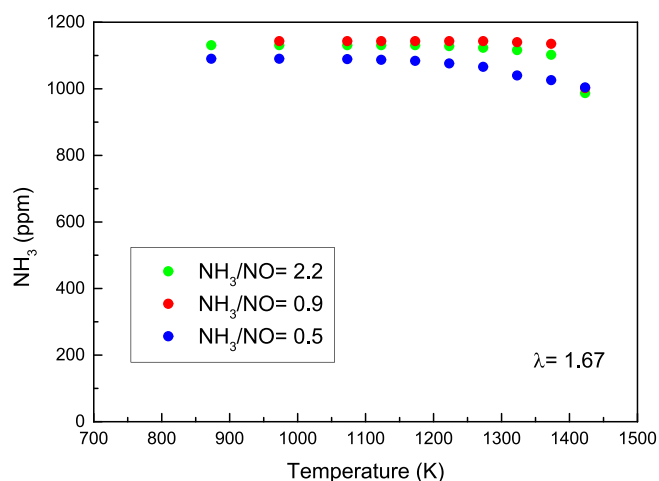


Fig. 10. NH_3 concentration as a function of temperature for different NH_3/NO ratios at the low gas residence time, $195/T(\text{K})$ s. Sets 11, 9 and 12 in Table 1.

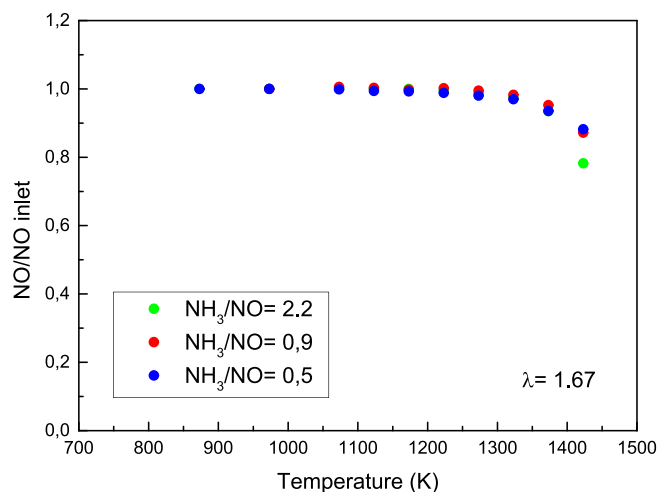


Fig. 11. Normalized NO concentration ($\text{NO}/\text{NO inlet}$) as a function of temperature for different NH_3/NO ratios at the low gas residence time, $195/T(\text{K})$ s. Sets 11, 9 and 12 in Table 1.

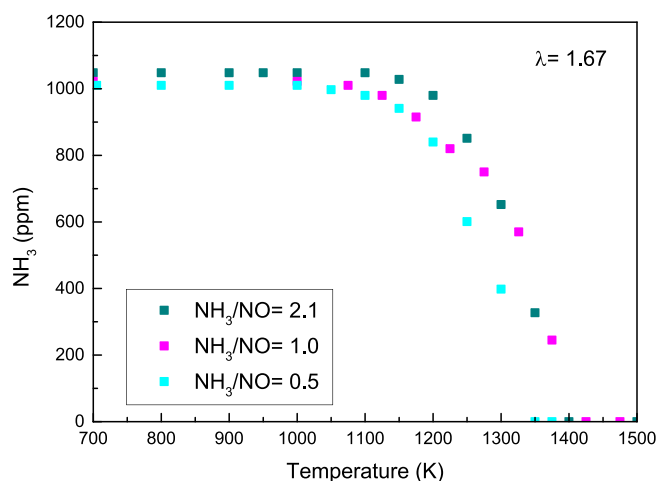


Fig. 12. NH_3 concentration as a function of temperature for different NH_3/NO ratios at the high gas residence time, $3100/T(\text{K})$ s. Sets 16, 14 and 17 in Table 1.

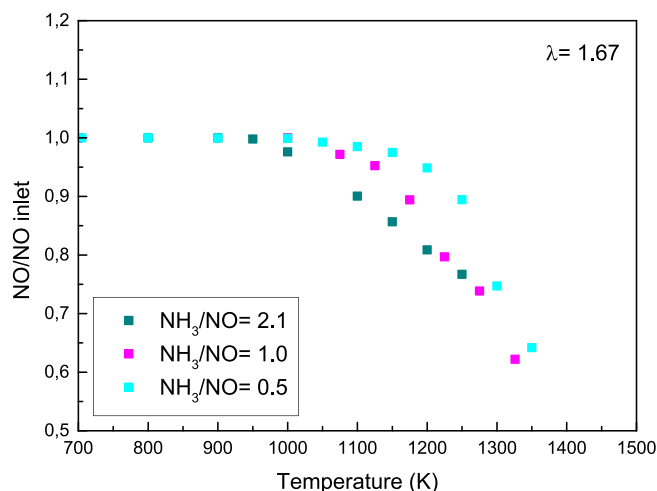


Fig. 13. Normalized NO concentration ($\text{NO}/\text{NO inlet}$) as a function of temperature for different NH_3/NO ratios at the high gas residence time, $3100/T(\text{K})$ s. Sets 16, 14 and 17 in Table 1.

has been carried out at atmospheric pressure using two different experimental set-ups, including respectively quartz and ceramic tubular flow reactors that allow to work in different ranges of temperature (up to 1500 K) and gas residence time. Different oxygen stoichiometries, from pyrolysis to significantly fuel-lean, were considered ($\lambda = 0$ to 3.33). The experimental results have been interpreted with an updated literature detailed chemical-kinetic mechanism.

The results obtained have allowed to determine that the presence of a CO_2/Ar atmosphere has an effect on ammonia oxidation compared to what happens in a N_2 atmosphere. Presence of CO_2 shifts the onset of ammonia conversion to lower temperatures and slows down its conversion at the higher temperatures studied. Presence of CO_2 is seen to induce a complex interaction of NH_3 with the O/H radical pool or with CO_2 , and thus affects the main conversion channels of ammonia evolution, and thus affects the conversion of ammonia.

In the presence of CO_2 , conversion of ammonia is favored as the availability of oxygen increases. Both NO and N_2 are formed from NH_3 , while N_2O and NO_2 are found to be negligible under the studied conditions. However, a number of nitrogen species, in very low concentrations, seems to be formed, according to non-closure of the nitrogen balance at high temperatures and to model calculations.

Presence of NO in the NH_3/CO_2 reaction system results in the

promotion of NH_3 conversion under fuel-rich conditions, while it inhibits the onset of the conversion initiation. Under the studied conditions, NO is reduced by action of NH_2 radicals through the well-known SNCR reactions.

Direct interaction of CO_2 and NH_3 plays a role under given conditions, in particular when those reactants are the dominant ones and the gas residence time is high. However, in the presence of increasing NO concentrations, the impact of the CO_2 atmosphere decreases. The complex observations and behavior attributed to the CO_2 presence is an indication that further studies dealing with the impact of a CO_2 atmosphere by comparison to a N_2/air atmosphere may be of interest.

Even though further work is still necessary in order to predict with precision the different species, the detailed kinetic mechanism used in calculations is able to reproduce the main trends observed experimentally, as well as the ammonia concentration profiles.

CRedit authorship contribution statement

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

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.

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