



Full Length Article

Conversion of NH₃/CO/NO/CO₂ mixturesMaría U. Alzueta^{*}, Iris Salas

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ABSTRACT

The present work addresses the impact of the presence of both CO and NO during the conversion of NH₃ using CO₂ or N₂/Ar as bath gas, which would correspond to oxy-fuel or conventional air fuel combustion processes respectively. The variation of temperature and oxygen excess ratio is studied in a flow reactor setup at atmospheric pressure. Experimental results have been simulated with a literature detailed kinetic mechanism and the main observations have been discussed. The main results indicate that the effect of the presence of CO is less important than in other reactive systems. Conversion of NH₃ is almost insensitive to the presence of CO, and the temperature regime for NH₃ conversion is only significantly affected under fuel-lean conditions. The present results extend the experimental database on ammonia conversion, for different mixtures and conditions, and contribute to evaluate the possibilities of improving the ignition of this compound.

1. Introduction

Ammonia is gaining a considerable interest in the recent years, both as a carrier gas but also as carbon free fuel e.g., [1–4]. Nowadays, progressive decarbonisation of the society is a must and ammonia may help and play a crucial role. Compared to hydrogen, the use of ammonia exhibits advantages, such as the fact that it does not contain carbon in its composition and that is worldwide available because of its extensive use mainly in the fertilizer industry and also in other applications. Additionally, ammonia can ideally be burned producing molecular nitrogen and water as products. However, in the practice, it is likely that ammonia will produce nitrogen oxides from its oxidation, mainly nitric oxide under combustion conditions e.g., [5–8].

A number of strategies and mixtures for the use of NH₃ as combustible are being considered nowadays, such as oxy-fuel combustion processes, which are addressed in the present work by the consideration of a high CO₂ environment. Biogas may contain significant amounts of NH₃ additionally to CO₂, and thus both components can be present together within the combustion device if biogas is used as a fuel. Previous works have concentrated on the effect that high amounts of CO₂ may imply in the conversion and oxidation of nitrogen species, such as NH₃ and its mixtures [9–12] or HCN [13,14]. Also, the presence of CO₂ may affect the formation of pollutants. CO₂ in high concentrations may change the global concentration of the radical pool, as well as the specific concentration of the different O and H containing radicals. One of the more relevant reactions involving CO₂ under combustion conditions is:



(r1) is a chain propagating reaction which converts OH radicals into H radicals. H radicals react effectively with oxygen through:



which would contribute to replenish the radical pool. In the presence of high amounts of CO₂, the reverse reaction, i.e. CO₂ + H ⇌ CO + OH (−r1), can be relevant. The occurrence of (−r1) may act to limit the radical pool because it competes with (r2), a chain branching reaction, and the global result is the diminution of the conversion of reactants. In this context, the joint presence of significant amounts of CO, coming either from the CO₂/CO equilibrium or from the incomplete combustion of carbon fuels in NH₃/hydrocarbon mixtures, may also have an effect.

Literature works have addressed the impact of the presence of either CO₂ or CO in the conversion of reactants e.g. [15–17], and the authors indicate a complex interaction of those species with the radical pool, interaction that is very dependent on the specific experimental conditions.

Complexity of the interactions may increase in the presence of NO, which can originate from the oxidation of NH₃ in significant amounts. NO is known to be an important sensitizing agent e.g. [18–21], and can also interact with NH₃ through selective non-catalytic reactions (SNCR) e.g. [22–26], which may be affected by the presence of significant amounts of CO and/or CO₂ e.g. [27,28].

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In this context, the present work aims to perform a systematic study of the presence and impact of CO, CO₂ and NO on NH₃ oxidation. Additionally, the impact of the different operating conditions on NO reduction is evaluated. The results may be of interest for practical applications of oxy-fuel combustion of NH₃, biogas combustion and for NO minimization strategies while using NH₃ as a carbon free fuel. The experimental results obtained are simulated with a literature mechanism and the main observations and findings are discussed.

2. Experimental methodology

Experiments of NH₃ oxidation at atmospheric pressure and different temperatures have been performed in the absence and presence of CO₂, CO and NO, in an experimental set-up, that has been used with success in a number of works. The setup includes a tubular quartz flow reactor, and its detailed description can be found elsewhere e.g. [10,29]. Reactants (NH₃, CO, NO, O₂ and H₂O), diluted either in a CO₂/Ar or a N₂/Ar atmosphere, are fed from gas cylinders using mass flow controllers. Water is fed by saturation of a N₂ or Ar stream. Since similar results are obtained when using N₂ and Ar for similar conditions [30], no significant influence of using either N₂ or Ar to balance is expected. When possible, Ar has been used as bath gas, with the aim of quantifying the amount of molecular nitrogen formed from NH₃ and NO with precision, so nitrogen balances can be done. Gases are directed to the reaction zone through four heated separate streams, as in Alzueta et al. [31], to avoid previous interaction of reactants. Then, the four streams are mixed at the entrance of reaction zone. The reaction zone has an internal diameter of 0.87 cm and a length of 20 cm. The reactor is situated within an electrical furnace which allows us to reach temperatures up to 1500 K with a flat temperature profile within ± 5 K, by means of three independently heated resistances. At the outlet of the reaction zone, reaction is quenched by external air with no contact with the outlet gases. The outlet stream is led to the analysis system, where the gas products are analyzed using a gas micro-chromatograph which includes thermal conductivity detectors for NH₃, O₂, H₂, N₂ and N₂O quantification, and continuous infra-red analyzers for NH₃, NO, NO₂, and N₂O. Uncertainty is estimated to be 5 %, and not less than 5 ppm for the continuous analyzers and 10 ppm for the micro-chromatograph [8]. Additionally, the error has been calculated according to the standard pooled deviation of the data (the square root of the sum of the squares of the error), where the error does not depend on the temperature in the interval considered and it is an estimator of the experimental error associated with the oxidation of NH₃. The pooled standard deviation has been calculated as ± 10 ppm.

Table 1 includes a description of the experimental conditions of the experiments. The experiments are performed at atmospheric pressure in the temperature range of 700–1450 K. The flow rate used is approximately 1 L (STP)/min, which results in a residence time (t_r) expressed as a function of temperature, as shown in Tables 1 and 2. The stoichiometry, i.e. oxygen excess ratio, (λ) is defined as the ratio between the

oxygen available for reaction and the stoichiometric oxygen, in the following reaction:



In Table 1, experiments 1, 5, 8 and 11 are performed using nitrogen as bath gas and have been taken from the work of Abián et al. [8]. Those experiments include the variation of the oxygen excess ratio during the oxidation of NH₃ in the absence of CO. Experiments done using CO₂ as bath gas but also in the absence of CO, have been taken from the work of Alzueta et al. [10], sets 2, 6, 9 and 12 of Table 1, and set 1 from the work of Alzueta et al. [32]. In the present work, we have done experiments using CO₂ as bath gas in the presence of approximately 1000 ppm CO, and correspond to sets 3, 7, 10 and 13 of Table 1. Additionally, we also performed one experiment in which the concentration of CO was doubled to approximately 2000 ppm, set 4 of Table 1.

Table 2 reports the conditions for the experiments performed in the presence of NO. In this case, only experiments with CO₂ and argon as bath gas, representative of oxy-fuel or biogas combustion, have been included. For comparison with experimental results obtained in the study of NH₃/NO mixtures in the absence of CO [10], sets 2, 4 and 6 of Table 2, we have done experiments in the presence of both CO and NO, sets 1, 3, 5, and 7 of Table 2. New performed experiments in the present work are denoted as “pw” (present work) in both tables.

3. Kinetic modelling

Simulations have been performed with a mechanism that was updated to simulate NH₃-CO mixtures [33]. No additional changes have been made to the mechanism in the present work. The mechanism is based on the reaction mechanism proposed by Glarborg et al. [26], and includes updates related to the amine chemistry based on the works of Stagni et al. [7], Glarborg and coworkers [34–38], and the authors [8,11]. As will be shown later, reaction pathways of NH₃ conversion under the conditions of the present work in the presence of both CO and CO₂ are similar to those found during the conversion of NH₃/CO₂ mixtures [33].

The Chemkin-Ansys software [39] has been used for calculations, choosing the PFR model. Thermodynamic data have been taken from the same sources as the different kinetic sub-mechanisms, and the rate constants for the reverse reactions were computed from the forward rate constants and the equilibrium constants.

4. Results and discussion

The presence of high amounts of CO₂, as happens during oxy-fuel combustion or biogas combustion, can affect the oxidation behavior of species. CO₂ modifies the radical pool since it competes with O₂ for hydrogen radicals through:



Table 1

Experimental conditions of the experiments in the absence of NO. pw denotes present work.

Set	NH ₃ (ppm)	NO (ppm)	CO (ppm)	O ₂ (ppm)	H ₂ O (%)	CO ₂ (%)	Ar (%)	N ₂ (%)	λ	t_r (s)	Source
1	1149	0	0	0	0	0	0	99.89	0	195/T(K)	[21]
2	1084	0	0	0	0	99.90	0	0	0	195/T(K)	[32]
3	1113	0	1132	0	0	85.00	14.78	0	0	195/T(K)	pw
4	1052	0	1965	0	0	96.70	3.00	0	0	180/T(K)	pw
5	971	0	0	298	0	0	0	99.89	0.41	195/T(K)	[21]
6	923	0	0	231	0.6	74.28	25.00	0	0.33	195/T(K)	[10]
7	1024	0	1071	417	0	82.20	17.50	0	0.32	177/T(K)	pw
8	976	0	0	780	0	0	0	99.82	1.06	195/T(K)	[21]
9	906	0	0	793	0.6	74.22	25.00	0	1.17	195/T(K)	[10]
10	1080	0	1158	1250	0	77.50	22.13	0	1.05	177/T(K)	pw
11	885	0	0	3517	0	0	0	99.56	5.30	195/T(K)	[21]
12	1159	0	0	2898	0.6	74.03	25.00	0	3.33	195/T(K)	[10]
13	1030	0	1110	6250	0	46.80	52.47	0	5.15	175/T(K)	pw

Table 2

Experimental conditions of the experiments in the presence of NO. pw denotes present work.

Set	NH ₃ (ppm)	NO (ppm)	CO (ppm)	O ₂ (ppm)	H ₂ O (%)	CO ₂ (%)	Ar (%)	N ₂ (%)	λ	t_r (s)	Source
1	1002	997	996	0	0	75.0	24.70	0	0	174/T(K)	pw
2	1125	1005	0	281	0.6	74.16	25.00	0	0.33	195/T(K)	[32]
3	1067	915	1039	443	0	72.00	27.65	0	0.33	174/T(K)	pw
4	1177	1010	0	1030	0.6	74.10	24.98	0	1.17	195/T(K)	[32]
5	1082	933	1076	1450	0	77.00	22.55	0	1.13	176/T(K)	pw
6	1122	995	0	2805	0.6	73.94	24.97	0	3.33	195/T(K)	[32]
7	974	970	945	6605	0	73.00	27.95	0	5.50	174/T(K)	pw



Both reactions produce OH radicals, which are important for the initiation of NH₃, e.g.:



While (r2) is a chain branching reaction, that can be followed by reaction $\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}$ (r5) which increases the concentration of the active OH radicals, (–R1) is chain propagating, thus keeping the concentration of radicals. As a consequence of this, the presence of CO₂ may strongly determine the maximum concentration of the radical pool that can be achieved.

On the other hand, the presence of high amounts of CO, both produced during the combustion of carbon fuels and from the CO/CO₂ equilibrium, may play as well a role in the conversion of NH₃. Under combustion conditions, CO is mainly consumed through (r1), followed by reaction (r2); and therefore the concentration of OH radicals is

determined by the extent of CO oxidation. The presence of CO is known to act as a promoter of combustion because of the sequence (r1) → (r2) → (r5) e.g. [20,38].

In the presence of high amounts of CO₂, reaction (r1) is limited because of the minor availability of OH radicals because reaction (r2), followed by (r5), are partly limited because of the occurrence of reaction (r1) in the reverse direction, i.e. (–r1).

The effect of high CO₂ concentrations mainly results in a significant inhibition of CO conversion, both in the absence and presence of water vapor. Therefore, the joint presence of significant amounts of CO and CO₂ together may produce different behaviors depending on the relative proportion of these species and the presence of other reactants, as NH₃ in the present work.

Fig. 1 (a, b, c) shows the concentration profiles of NH₃, CO and O₂ for the different oxygen excess ratios studied ($\lambda = 0, 0.32, 1.05$, and 5.15) as a function of temperature in a CO₂/Ar atmosphere. Experimental results are represented by symbols and model calculations by lines. Additionally, Fig. 1d includes comparison of the normalized NH₃ concentrations

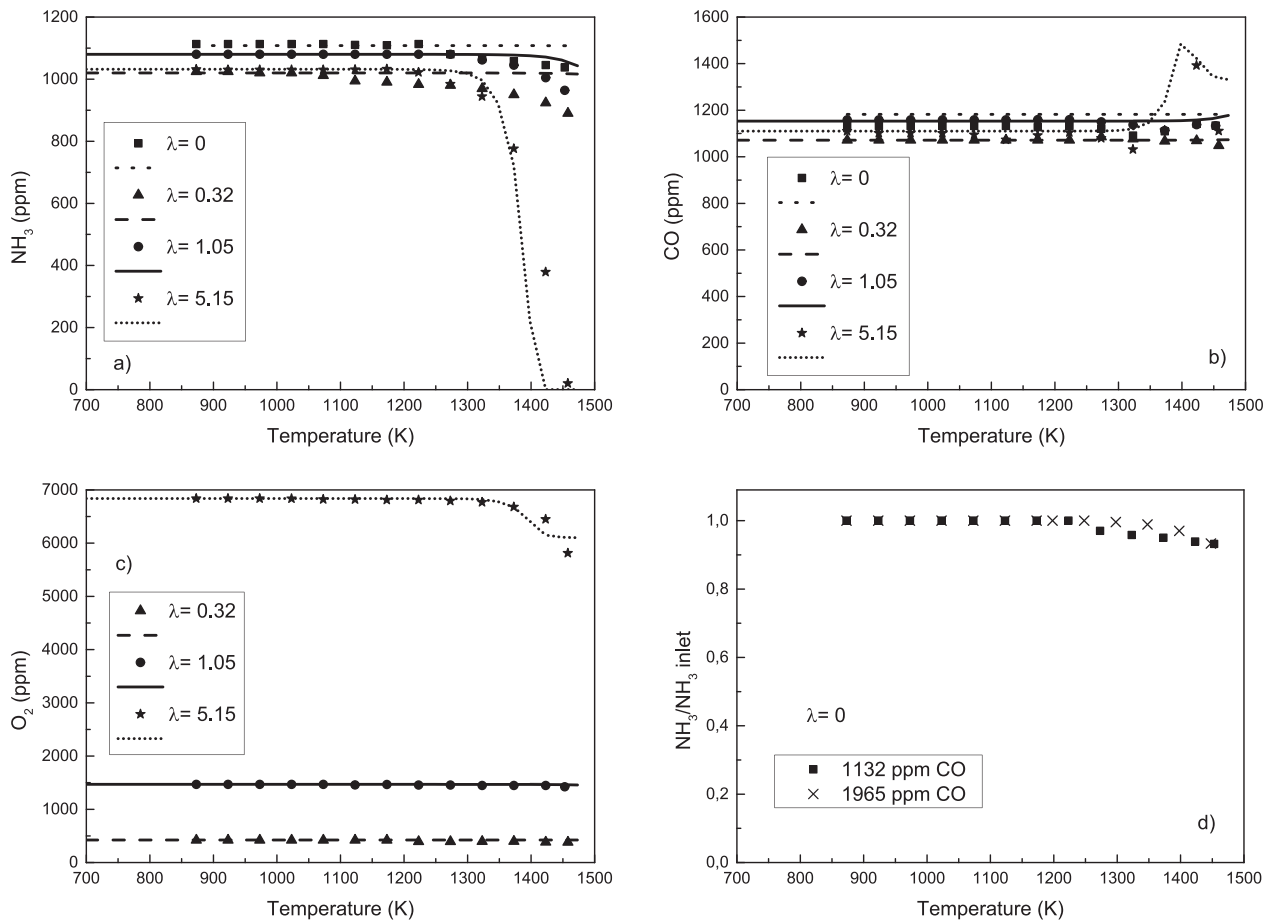


Fig. 1. NH₃ (a), CO (b) and O₂ (c) concentration profiles versus temperature for different oxygen excess ratios, in the presence of around 1000 ppm CO in a CO₂/Ar atmosphere, and normalized NH₃/NH₃ inlet (d) for two different CO concentrations. Sets 3, 7, 10, 13, and 4 of Table 1.

for two different CO concentrations, one double of the other. No appreciable formation of nitrogen products other than N_2 is found under the studied conditions, which coincides with model predictions.

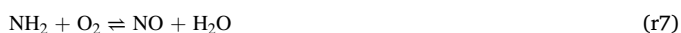
Conversion of NH_3 occurs at lower temperatures as the stoichiometry is increased, even though under the studied conditions, only full conversion of NH_3 is found at the highest oxygen excess ratio of $\lambda = 5.15$ and temperatures around 1450 K, Fig. 1a. Similar observations can be done for CO and O_2 (Fig. 1b and 1c respectively), where only an appreciable conversion of O_2 and CO is seen above 1400 K.

The effect of the CO concentration is also negligible under the studied conditions, Fig. 1d, where doubling the CO concentration does not produce any significant influence on NH_3 conversion.

If we compare the impact of the presence of CO during the combustion of NH_3 under high CO_2 concentrations, we can see that, in general, is significant. Fig. 2a and b show respectively the comparison of the results obtained both in the absence and presence of approximately 1000 ppm CO on the conversion of NH_3 in the Ar/ CO_2 environment. Comparison of Fig. 2b with Fig. 2a further allows to see the impact of a N_2/CO_2 atmosphere compared to Ar.

In general, it is seen a very little impact of the presence of CO under pyrolysis conditions independently on the bath gas (Ar or N_2 , in the presence of not of water vapor), coinciding with what was observed in the works of Benés et al. [30] and Alzueta et al. [32] for the pyrolysis and oxidation of ammonia respectively. For oxygen excess ratios of $\lambda = 0.3$ and higher, the presence of CO and the increase in the oxygen availability result in a promotion of NH_3 conversion compared to the absence of CO. This happens both in the CO_2/Ar and N_2 atmospheres, slightly more pronounced in the presence of CO_2 . This indicates the importance of the radical pool concentration and speciation driven by the local conditions of NH_3 combustion, as well as the complex interaction of radicals with CO, CO_2 , H_2O and NH_3 , which regulates the conversion process. The main general reaction pathways for NH_3 conversion are found to be the same as in previous works [33].

NH_3 oxidation is known to be initiated by reaction with OH radicals, $NH_3 + OH \rightleftharpoons NH_2 + H_2O$ (r4). (r4) generates NH_2 radicals, which can further evolve either to N_2 or to NO, i.e.:



Since NO is likely formed from NH_3 oxidation at the high temperatures of combustion, e.g. (r7), the study of the presence of NO in the $NH_3/CO/CO_2$ system is of interest. Under these conditions, the interaction between NH_3 and NO may occur through reactions representative of the selective non-catalytic reaction (SNCR) process, i.e.:



These SNCR reactions are favored under oxygen excess conditions and intermediate temperatures e.g. [1,19,22,24,25].

Therefore, in the present work, we have done experiments adding approximately 1000 ppm of NO to the $NH_3/CO/CO_2$ system, as seen in Table 2. While NO is an undesired outcome of burning NH_3 , the joint presence of NH_3 and NO may become an opportunity for the minimization of NO if present. Interaction between NH_3 and NO may result in the reduction of around 80 % of the NO emission under given conditions e.g. [40]. These high reduction percentages may vary, mostly diminish, depending on the specific temperature and local O_2 conditions. The maximum NO reductions by NH_3 in the SNCR or Thermal DeNO_x process occur under excess oxygen conditions and temperatures around 1000–1200 K e.g. [24–26]. An advantage of this reduction mechanism is that it proceeds mole to mole, so a small fraction of NH_3 is very effective to reduce NO. In previous works [11,28,32] we analyzed the reduction of NO by NH_3 under a variety of conditions, both in conventional and oxy-fuel combustion systems, and the main results indicate that presence of NO acts to promote NH_3 conversion under fuel-rich conditions, with an effective reduction of NO through SNCR reactions also under these conditions. Under oxy-fuel combustion conditions, the presence of NO inhibits the conversion of NH_3 compared to the air conventional conditions, which can be a drawback for the application of oxy-fuel combustion to burn NH_3 or NH_3 mixtures.

However, compared to the results in the absence of CO [32], the presence of NO has been found, in the present work, to exhibit a different behavior. In our previous work, we found that, in the absence of CO, NO acted to promote NH_3 conversion under fuel-rich conditions, while it inhibited NH_3 conversion as the O_2 availability increased. This is clearly not seen in the presence of significant amounts of CO, which seem to smooth the observed behaviors. This occurs because CO acts to increase the O/H radical pool through the following chain branching sequence: $CO + OH \rightleftharpoons CO_2 + H$ (r1) followed by $H + O_2 \rightleftharpoons OH + O$ (r2) and $O + H_2O \rightleftharpoons OH + OH$ (r5).

Fig. 3 (a,b,c,d,e) shows the results of NH_3 , CO, O_2 , NO and N_2 in the presence of 1000 ppm of CO and a similar value of the concentration of NO. Even though it is not shown, also small amounts of H_2 are produced under the studied conditions, lower than 25 ppm in any case. The present results indicate that NO acts to boost significantly the conversion of NH_3 and that of CO to CO_2 , compared to the results in the absence of NO (Fig. 1) for the fuel-leaner conditions considered. However, no significant promoting effect of NO is found for stoichiometric and

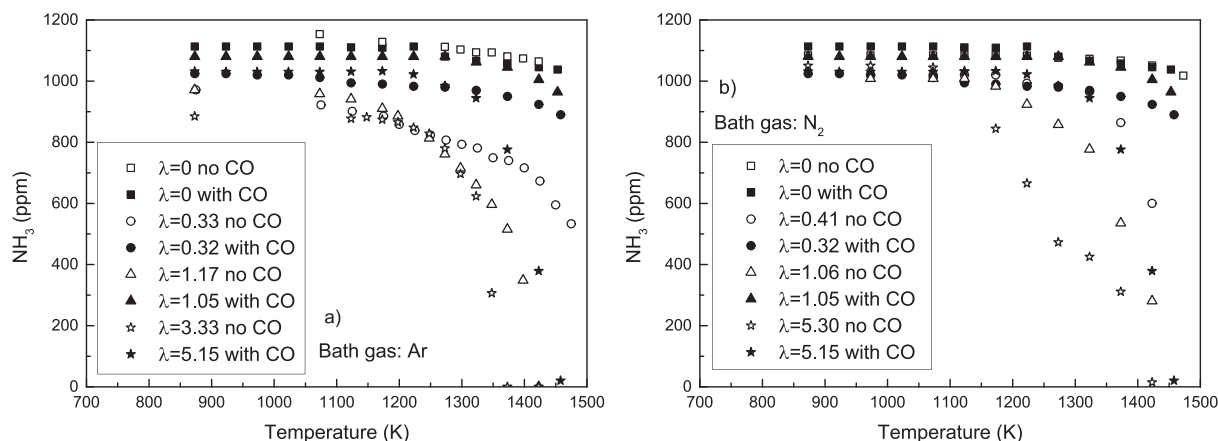


Fig. 2. Comparison of the NH_3 profiles in the absence (open symbols) and the presence of 1000 ppm CO (solid symbols) for the different oxygen excess ratios considered and as a function of the temperature. Experiments in the absence of CO in Fig. 2a are performed with Ar as bath gas (Sets 2, 3, 6, 7, 9, 10, 12, and 13 of Table 1), while in Fig. 2b, the bath gas is N_2 (Sets 1, 2, 5, 7, 8, 10, 11 and 13 of Table 1).

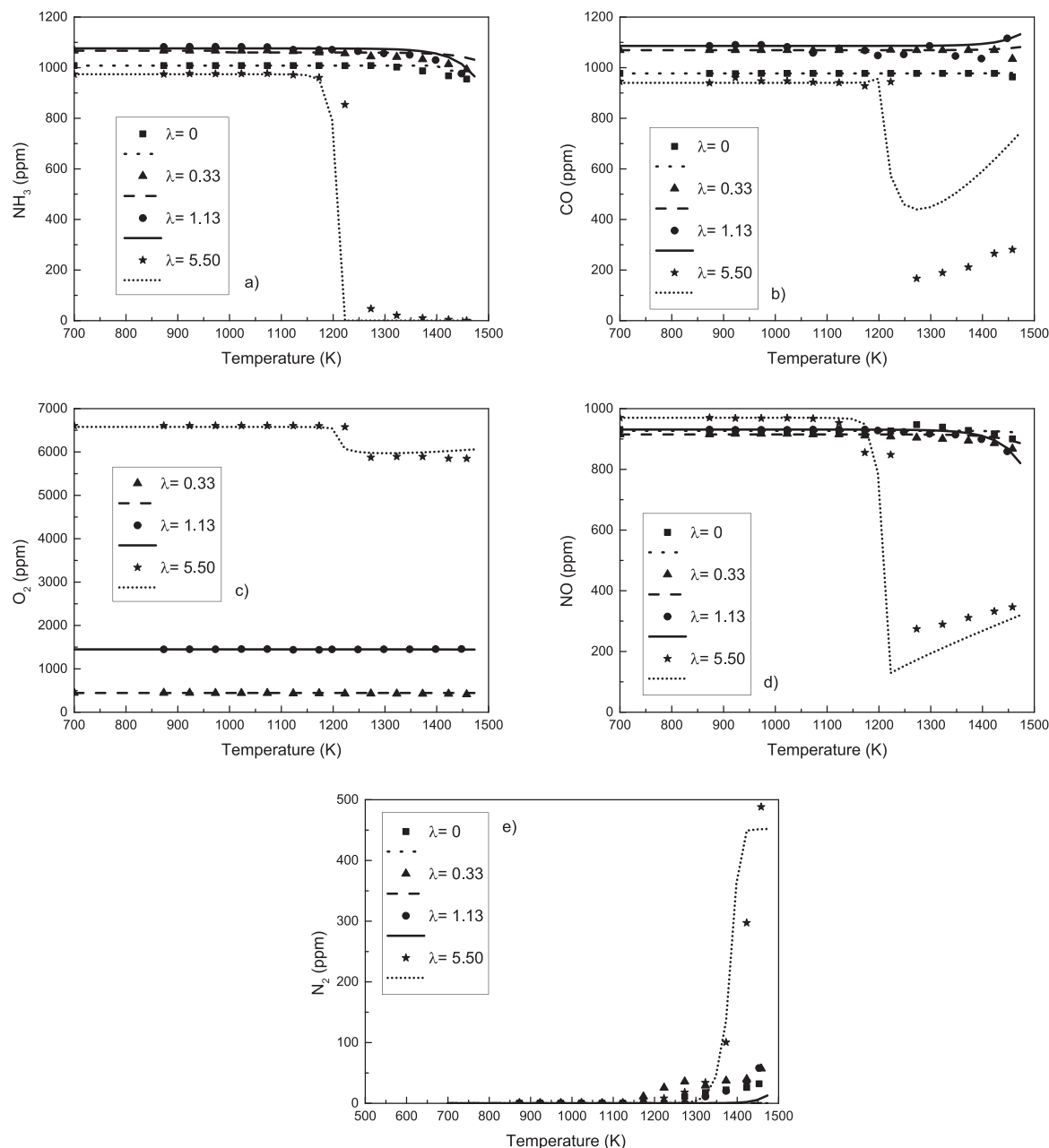


Fig. 3. Concentration profiles of NH_3 (a), CO (b), O_2 (c), NO (d) and N_2 (e) versus temperature for different oxygen excess ratios in the presence of 1000 ppm CO and 1000 ppm NO in a CO_2/Ar atmosphere. Sets 1, 3, 5, 7 in Table 2.

substoichiometric conditions, contrarily to what was observed in the absence of CO [32]. The model used for calculations, represented as lines, does reproduce, in general, the experimental observations.

It is interesting to remark that the promoting effect of an undesired pollutant as NO brings a positive outcome for the use of NH_3 as a fuel, at least under oxidizing conditions. The inevitable formation of NO will help to decrease the ignition temperature of NH_3 , which is one of the main drawbacks for using NH_3 as a fuel. Additionally, since NH_3 will be combusted under overall air excess conditions, both formation and reduction of NO will occur, and interesting synergies will likely happen.

For the leanest oxygen excess ratio tested, i.e. $\lambda = 5.5$, NH_3 conversion starts at approximately 1200 K and reaches full conversion around 1250 K. The NH_3 conversion onset coincides with the decrease in CO , O_2 and NO concentrations, and it is quite well predicted by the model. It is remarkable that the reduction of NO reaches its maximum value at approximately 1200 K, coinciding with the decrease of NH_3 , with

around 80 % conversion, and decreases as temperature increases. NO reduction is over 60 % at the highest temperature studied, 1450 K.

As seen in Fig. 3e, the main nitrogen species formed during the combustion of the mixtures studied is molecular nitrogen, which is confirmed by the model.

Similarly to what has been shown in Fig. 2 in the absence of NO , we can observe the effect of the presence of CO while burning mixtures of NH_3 and NO under high CO_2 concentrations. Since bath gas was found to have a negligible effect on the results, Fig. 4 does not make a difference between argon or nitrogen as balance gas, and includes the concentration profiles of NH_3 for different oxygen excess ratios as a function of temperature both in the absence and presence of CO , with a NO concentration of approximately 1000 ppm in every experiment. We can see that the effect of the presence of CO is almost negligible for the richest oxygen excess ratios up to a value of $\lambda \sim 1$. Only for the leanest oxygen excess ratios considered, $\lambda = 5.50$ in the presence of CO or 3.33 in the

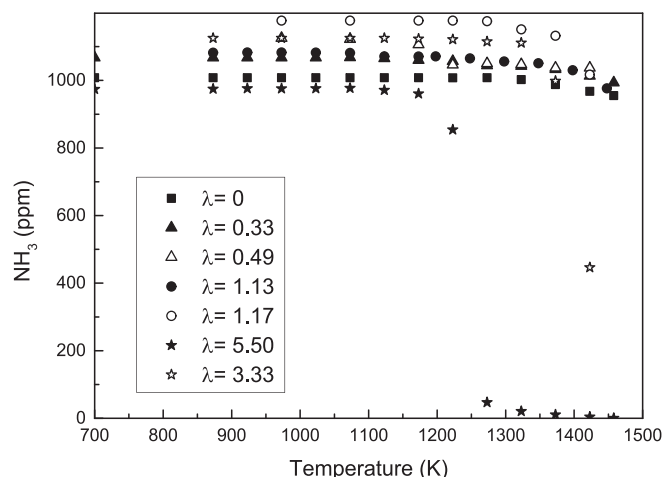


Fig. 4. Comparison of the NH_3 profiles in the absence of CO (open symbols), Sets 2, 4 and 6 of Table 2, and the presence of 1000 ppm CO (solid symbols), Sets 1, 3, 5, and 7 of Table 2 for the different oxygen excess ratios considered, in the presence of around 1000 ppm NO, and as a function of the temperature.

absence of CO, a difference between NH_3 profiles can be observed, with a clear promotion of the NH_3 conversion in the presence of CO. In the latter case, full conversion of NH_3 is achieved above 1300 K while this happens above 1450 K in the absence of CO (not reached in the present experiments). The observed effect of CO on the promotion of NH_3 conversion is lower than in the absence of NO, See Fig. 2. The reason is that CO consumes H radicals, through the dominance of reaction $\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH}$ (r1) under rich conditions, while only when O_2 availability is high, competition with $\text{O}_2 + \text{H} \rightleftharpoons \text{O} + \text{OH}$ (r2) starts to feed the radical pool and contributes to the promotion of NH_3 oxidation. Additionally, NO participates in a number of reactions with the radical pool which limit their availability to interact with CO, diminishing thus the promoting effect of CO. It has to be mentioned that even though the conditions compared are not exactly equal in stoichiometry ($\lambda = 5.5$ in the presence of CO and 3.33 in the absence of CO), probably this variation in λ does not make a significant difference related to the main observations and trends obtained, but only on the specific values of the concentrations, following the observations of similar studies e.g. [8,11] and model calculations.

In order to further evaluate the good performance of the experiments, as well as to know if the species measured are the right ones, we have done carbon and nitrogen balances in the different experimental results. The carbon balances include CO and CO_2 and have closed in all cases at around 100 % and thus are not shown. The nitrogen balances close also very well, even though small discrepancies are observed. Fig. 5 shows, as an example, the nitrogen balance for the experiments including NO. Species included in the balance, both in experiments and in model calculations, are: NH_3 , NO, and N_2 . N_2O , NO_2 , HCN or HNCO are not included because those species have not been detected in appreciable quantities at any condition. As seen in Fig. 5, the nitrogen balance overall closes very well, with small discrepancies for the highest oxygen excess ratio studied. The good agreement between experimental results and calculations indicates that the species quantified are clearly the dominant ones, and that N_2O is negligible. There is a certain discrepancy in the literature in relation to N_2O : it has been reported to be significant in some works [41,42], mainly in flames, while other works have found it as negligible e.g. [43] and in the present work.

5. Conclusions

The impact of using either oxy-fuel or air combustion conditions on the conversion of NH_3/CO mixture on the conversion of NH_3 and formation of products has been studied from experimental and simulation

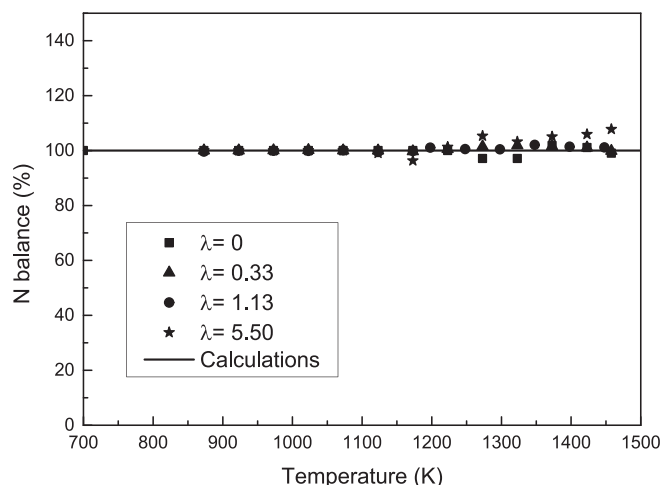


Fig. 5. Nitrogen balance (as percentage) of the experiments performed in the presence of around 1000 ppm NO and CO. Symbols correspond to experimental data and the line to model calculations. Sets 1, 3, 5, and 7 of Table 2.

study points of view. The study has been performed at atmospheric pressure under carefully controlled conditions, varying important variables such as temperature and oxygen excess ratio and NH_3/CO ratio for given conditions. 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 difficulty of NH_3 ignition has been observed under the studied conditions, independently of the presence of either or both CO and NO. Conversion of NH_3 is only significant under fuel lean conditions under the conditions of the present work. Variation of the CO concentration has an insignificant effect on the conversion of NH_3 .

The presence of NO during the conversion of $\text{NH}_3/\text{CO}/\text{CO}_2$ mixtures has a strong impact only under lean conditions, where the NH_3 conversion is significantly shifted to lower temperatures in the presence of NO. Under these conditions, NO is significantly reduced around 80 % through SNCR reactions. Almost no effect of the presence of NO is found for stoichiometric and fuel-rich conditions, indicating little or no interaction between NH_3 and NO under these conditions.

In the presence of CO, little differences of the CO_2/Ar or N_2/Ar environment have been found under the studied conditions, lower than what was found in the absence of CO in literature works.

Similarly to what was observed in the absence of CO, no significant direct interaction of NH_3 and CO or CO_2 has been found for the low concentrations of reactants used in the present experiments, since no HCN or HNCO are found as final products. Other species such as N_2O or NO_2 have not been either detected in appreciable concentrations.

The literature detailed kinetic mechanism used in calculations is able to reproduce the main trends observed experimentally, as well as the NH_3 and products concentration profiles.

CRediT authorship contribution statement

María U. Alzueta: Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Conceptualization. **Iris Salas:** Validation, Methodology, Investigation.

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.

Data availability

Data will be made available on request.

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References

- Mathieu O, Petersen EL. Experimental and modeling study on the high-temperature oxidation of ammonia and related NO_x chemistry. *Combust Flame* 2015;162: 554–70.
- Kobayashi H, Hayakawa A, Somaratne KDKA, Okafor EC, Ekenechukwu C. Science and technology of ammonia combustion. *Proc Combust Inst* 2019;37: 109–33.
- Valera-Medina A, Xiao H, Owen-Jones M, David WIF, Bowen PJ. Ammonia for power. *Prog Energy Combust Sci* 2018;69:63–102.
- Valera-Medina A, Amer-Hatem F, Azad AK, Dedoussi IC, de Joannon M, Fernandes RX, et al. Review on ammonia as a potential fuel: from synthesis to economics. *Energy Fuel* 2021;35:6964–7029.
- Miller JA, Smooke MD, Green RM, Kee RJ. Kinetic modeling of the oxidation of ammonia in flames. *Combust Sci Technol* 1983;34:149–76.
- Barbas M, Costa M, Vranckx S, Fernandes RX. Experimental and chemical kinetic study of CO and NO formation in oxy-methane premixed laminar flames doped with NH₃. *Combust Flame* 2015;162:1294–303.
- Stagni A, Cavallotti C, Arunthanayothin S, Song Y, Herbinet O, Battin-Leclerc F, et al. An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia. *React Chem Eng* 2020;5:696–711.
- Abián M, Benés M, de Goñi A, Muñoz B, Alzueta MU. Study of the oxidation of ammonia in a flow reactor. Experiments and kinetic modeling simulation. *Fuel* 2021;300:120979.
- Mendiara T, Glarborg P. NO reduction in oxy-fuel combustion of methane. *Energy Fuel* 2009;23:3565–72.
- Alzueta MU, Giménez-López J, Mercader VD, Bilbao R. Conversion of NH₃ and NH₃-NO mixtures in a CO₂ atmosphere. A parametric study. *Fuel* 2022;327: 125133.
- Alzueta MU, Ara L, Mercader V, Delogu M, Bilbao R. Interaction of NH₃ and NO under combustion conditions. Experimental flow reactor study and kinetic modeling simulation. *Combust Flame* 2022;235:111691.
- Sun ZJ, Deng YW, Song SB, Yang JZ, Yuan WH, Qi F. Experimental and kinetic modeling study of the homogeneous chemistry of NH₃ and NO_x with CH₄ at the diluted conditions. *Combust Flame* 2022;243:112015.
- Giménez-López J, Millera A, Bilbao R, Alzueta MU. HCN oxidation in an O₂/CO₂ atmosphere: an experimental and kinetic modeling study. *Combust Flame* 2010; 267–276:112015.
- Giménez-López J, Millera A, Bilbao R, Alzueta MU. Interactions of HCN with NO in oxy-fuel combustion. *Energy Fuel* 2015;29:6593–7.
- Glarborg P, Bentzen LLB. Chemical effects of a high CO₂ concentration in oxy-fuel combustion of methane. *Energy Fuel* 2008;22:291–6.
- Abián M, Giménez-López J, Bilbao R, Alzueta MU. Effect of different concentration levels of CO₂ and H₂O on the oxidation of CO. Experiments and modelling. *Proc Combust Inst* 2011;33:317–23.
- Ding C, Li P, Wang K, Shi G, Wang F, Liu Z. Experimental and kinetic study on the oxidation of syngas-ammonia under both N₂ and CO₂ atmospheres in a jet-stirred reactor. *Syngas Fuel* 2021;35:11445–56.
- Dagaut P, Mathieu O, Nicolle A, Dayma G. Experimental study and detailed kinetic modeling of the mutual sensitization of the oxidation of nitric oxide, ethylene, and ethane. *Combust Sci Technol* 2005;177:1767–91.
- Dagaut P. On the oxidation of ammonia and mutual sensitization of the oxidation of NO and ammonia: experimental and kinetic modeling. *Combust Sci Technol* 2022;194:117–29.
- Glarborg P, Kubel D, Kristensen PG, Hansen J, Dam-Johansen K. Interactions of CO, NO_x and H₂O under post-flame conditions. *Combust Sci Technol* 1995;111:461–85.
- Song Y, Marrodon L, Vin N, Herbinet O, Assaf E, Pittschen C, et al. The sensitizing effects of NO₂ and NO on methane low temperature oxidation in a jet stirred reactor. *Proc Combust Inst* 2019;37:667–75.
- Miller JA, Branch MC, Kee RJ. A chemical kinetic model for the selective reduction of nitric oxide by ammonia. *Combust Flame* 1981;43:81–98.
- Miller JA, Bowman CT. Mechanism and modeling of nitrogen chemistry in combustion. *Progr Energy Combust Sci* 1989;15:287–338.
- Glarborg P, Dam-Johansen K, Miller JA, Kee RJ, Coltrin ME. Modeling the thermal DeNO_x process in flow reactors. Surface effects and nitrous oxide formation. *Int J Chem Kinet* 1994;26:421–36.
- Miller JA, Glarborg P. Modeling the thermal DeNO_x process: closing in on a final solution. *Int J Chem Kinet* 1999;31:757–65.
- Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. Modeling nitrogen chemistry in combustion. *Prog Energy Combust Sci* 2018;57:31–68.
- Alzueta MU, Røjel H, Kristensen PG, Glarborg P, Dam-Johansen K. Laboratory study of the CO/NH₃/NO/O₂ system. Implications for hybrid reburn/SNCR strategies. *Energy Fuel* 1997;11:716–23.
- Alzueta MU, Abián M, Elvira I, Mercader VD, Sieso L. Unraveling the NO reduction mechanisms occurring during the combustion of NH₃/CH₄ mixtures. *Combust Flame* 2023;257:112531.
- Alzueta MU, Bilbao R, Finestra M. Methanol oxidation and its interaction with nitric oxide. *Energy Fuel* 2001;15:724–9.
- Benés M, Pozo G, Abián M, Millera A, Bilbao R, Alzueta MU. Experimental study of the pyrolysis of NH₃ under flow reactor conditions. *Energy Fuels* 2021;35: 7193–200.
- Alzueta MU, Glarborg P, Dam-Johansen K. Low temperature interactions between hydrocarbons and nitric oxide: an experimental study. *Combust Flame* 1997;109: 25–36.
- Alzueta MU, Mercader VD, Giménez-López J, Bilbao R. NH₃ conversion and NO reduction by NH₃ in N₂/Ar and CO₂ atmospheres. *Fuel* 2023;353:129212.
- Alzueta MU, Salas I, Hashemi H, Glarborg P. CO assisted NH₃ oxidation. *Combust Flame* 2023;257:112438.
- Glarborg P, Hashemi H, Cheskis S, Jasper AW. On the rate constant for NH₂ + HO₂ and third-body collision efficiencies for NH₂ + H (+M) and NH₂ + NH₂ (+M). *J Phys Chem A* 2021;125:1505–16.
- Marshall P, Rawling G, Glarborg P. New reactions of diazene and related species for modelling combustion of amine fuels. *Mol Phys* 2021;119:e1979674.
- Klippenstein SJ, Glarborg P. Theoretical kinetics predictions for NH₂+HO₂. *Combust Flame* 2022;236:111787.
- Glarborg P, Hashemi H, Marshall P. Challenges in kinetic modeling of ammonia pyrolysis. *Fuel Comm* 2022;10:100049.
- Glarborg P. The NH₃/NO₂/O₂ system: constraining key steps in ammonia ignition and N₂O formation. *Combust Flame* 2023;257:112311.
- Chemkin-ANSYS 18. ANSYS Inc.; 2019.
- Kasuya F, Glarborg P, Johsson JE, Dam-Johansen K. The thermal DeNO_x process. Influence of partial pressures and temperature. *Chem Eng Sci* 1995;50:1455–66.
- An Z, Zhang M, Zhang W, Mao R, Wei X, Wang J, et al. Emission prediction and analysis on CH₄/NH₃/air swirl flames with LES-FGM method. *Fuel* 2021;304: 121370.
- Lia S, Zhang S, Zhoua H, Rena Z. Analysis of air-staged combustion of NH₃/CH₄ mixture with low NO_x emission at gas turbine conditions in model combustors. *Fuel* 2019;237:50–9.
- Okafor EC, Somaratne KDKA, Ratthanana R, Hayakawa A, Kudo T, Kurata O, et al. Control of NO_x and other emissions in micro gas turbine combustors fuelled with mixtures of methane and ammonia. *Combust Flame* 2020;211:406–16.