



Conversion of methylamine in a flow reactor and its interaction with NO

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ABSTRACT

The conversion of methylamine (CH_3NH_2 , 1000 ppm) has been studied in an atmospheric-pressure flow reactor from both experimental and modeling points of view. Several values of the oxygen excess ratio (λ), from pyrolysis to fuel-lean conditions, have been tested, and a large number of different species have been quantified experimentally by three different diagnostic techniques: gas chromatography, Fourier Transform Infra-red spectroscopy (FTIR) and an infra-red NO analyzer. For the first time, the influence of NO addition (500 and 1000 ppm) on the stoichiometric oxidation of methylamine has also been experimentally evaluated, and the main products of such interaction have been identified. Results indicate that, unlike the little influence of oxygen availability on methylamine conversion, the presence of different concentrations of NO promotes methylamine oxidation at lower temperatures. A literature mechanism has been validated against the present experimental data since previous experimental works under these conditions are scarce. The largest discrepancies have been found for the formation of NH_3 and NO as oxidation products, which are under and overestimated by the model, respectively, and under pyrolysis conditions, where modification of the kinetic parameters for the reaction $\text{CH}_2\text{NH}_2 \rightleftharpoons \text{CH}_2\text{NH} + \text{H}$ from the original mechanism notably improves the agreement between experimental and simulated results.

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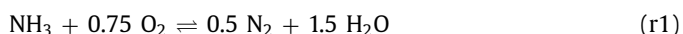
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1. Introduction

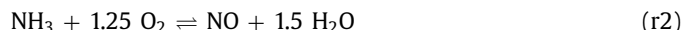
Ammonia is considered a valuable carbon-free energy vector, suitable as an alternative fuel for transportation [1]. It presents a high hydrogen density and boiling and condensation temperatures like propane, which makes it a promising hydrogen carrier [2]. Despite its enormous potential, there are some drawbacks that could limit its applicability, such as its narrow flammability limits or the high auto-ignition temperature [3].

With respect to pollutant emissions, ammonia may exhibit different behaviors. Ideally, ammonia can be burned in a benign way, producing only molecular nitrogen and water vapor as products, i.e.:



However, conversion of ammonia at high temperatures and in a combustion environment, with air excess, will likely result in the

formation of NO, through the global reaction (r2) and subsequently produce the emission of NO_x in the flue gasses.



Additionally, the joint presence of NH_3 and NO within the combustion chamber may result in their interaction, through reactions occurring in the selective non-catalytic (SNCR) process under given conditions. Several recent works have addressed this issue both in air and oxy-fuel combustion conditions [4–7]. The results indicate that an effective reduction of NO can happen depending on the specific conditions considered. Additionally, the presence of NO may influence the conversion of amine species.

While the combustion of ammonia is potentially possible (e.g. [8]), in the next future it is likely that ammonia will be mixed with other fuels which can act somehow as fuel enhancers or promoters. Methane [9,10] or hydrogen [11] have been proposed in a way to facilitate ammonia combustion in internal combustion engines. Also, the use of small amounts of promoters, such as dimethyl ether (DME) or diethyl ether (DEE) has been suggested with the aim of facilitating ammonia ignition (e.g., [12–14]). In all these cases, if NH_3 and carbon fuels are co-combusted, it is likely

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that methylamine (MEA, CH_3NH_2) may be found as an intermediate formed through the reaction of methyl and amino radicals [15], i.e.:



as mentioned by Mendiara and Glarborg [16] when modeling the conversion of NH_3/CH_4 mixtures in a CO_2 environment under flow-reactor conditions and identified experimentally in our recent work [17] when studying the conversion of NH_3/CH_4 mixtures at high pressures.

While the oxidation and pyrolysis of methylamine has been considered in the past, experimental studies on methylamine oxidation are still scarce in the recent past, where the diagnostic techniques available permit the precise quantification of many species that can be originated during MEA conversion. The interest on methylamine has been different along the time. While in the middle of the 20th century, it was focused on the conversion of substituted aliphatic compounds to analyze the influence of the hydrocarbon structure on the ease of oxidation (e.g. [18–21]), at the end of the past century, the interest relied either on the formation of NO_x from N-compounds present in fuels (e.g. [21–23]) or the use of amines as NH_3 -additives/derivatives as selective reduction agents in the Thermal De NO_x (SNCR) process [24–26]. Also, certain studies have addressed the study of methylamine under supercritical water conditions (e.g., [27,28]), mainly of interest for waste compounds destruction. Nowadays, the main interest comes from the investigations on the use of mixtures of ammonia with hydrocarbons, which interaction, as mentioned above, may result in the formation of organic amines, such as MEA.

Modeling of methylamine conversion has also been studied in parallel with the experimental works. Recently, Glarborg et al. [29] have developed a chemical kinetic mechanism for methylamine oxidation based on theoretical calculations and previous literature methylamine oxidation works on batch reactors, flow reactors, shock tubes and flames (Glarborg et al., [29] and references therein). Glarborg and coworkers [29] reported the lack of a wide experimental characterization useful to validate the model, as well as the need to carry out new experimental studies in the presence of NO (only qualitatively described).

In this context, the present work is focused on the analysis of methylamine oxidation from both experimental and modeling points of view. New well-controlled experiments have been performed in a quartz flow reactor, at atmospheric pressure, covering a wide range of temperatures and air excess ratios (from pyrolysis to fuel-lean conditions). Additionally, the effect of NO presence has been evaluated. Particular attention has been paid to the quantification of the different species. The study has been completed with a modeling analysis using the detailed chemical-kinetic mechanism from literature mentioned above [29].

2. Methodology

The experiments have been performed in an atmospheric-pressure set-up previously used by the research group to study the gas-phase oxidation of different compounds, among them, ammonia (e.g., [6,7,30]). Therefore, the experimental setup has been described in detail in previous works (e.g., [30,31]) and only the most relevant aspects will be highlighted below.

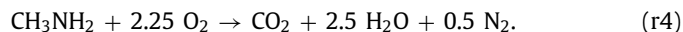
A controlled evaporator mixer (CEM) has been used to feed an aqueous solution of methylamine (40% by weight), supplied by Sigma Aldrich (extra pure), to the reaction system. The methylamine line is heated until the reactor entrance to avoid undesired condensation. The other reactants, O_2 and NO, and Ar to balance, are fed from gas cylinders. Gasses are kept in independent streams and only mixed at the inlet of the reaction zone. The reactor is

Table 1
Matrix of experimental conditions^a.

Set	CH_3NH_2 (ppm)	O_2 (ppm)	NO (ppm)	λ
1	905	–	–	0
2	1019	1779	–	0.78
3	994	2441	–	1.09
4	996	2615	–	1.17
5	1044	23,856	–	10.16
6	933	2485	490	1.18
7	721	2235	951	1.38

^a All the experiments have been conducted at atmospheric pressure in the 600–1375 K temperature range, with a total flow rate of 1 L (STP)/min and using Ar as bath gas. The molar ratio of MEA/ H_2O has been kept constant at around 2.59 (i.e., the one existing in the feed mixture).

placed within a three-zone electrically heated furnace ensuring an isothermal reaction zone (± 5 K) of 20 cm in length and 8.7 mm of diameter. The total flow rate has been kept constant at 1 L (STP)/min in all the experiments, resulting in a gas residence time within the reaction zone of t_r (s)=195/T(K). The experimental conditions are listed in Table 1. The oxygen excess ratio (λ) has been varied between pyrolysis ($\lambda=0$) and fuel-lean conditions ($\lambda\sim 10$) and has been determined considering the stoichiometric reaction (r4).



The gas stream at the outlet of the reactor has been analyzed using:

- A gas micro-chromatograph (Agilent 490) equipped with thermal conductivity detectors (TCD) and four different columns that allow the quantification of CH_3NH_2 , O_2 , N_2 , H_2 , H_2O , NH_3 , HCN, N_2O , CO and CO_2 . One of these columns, the so-called Volamine, is optimized for the analysis of volatile amines which also allows the detection of water, not trivial by gas chromatography. This is the first attempt we have made to analyze and quantify water using that column.
- A continuous infra-red NO analyzer (ABB, advance optima).
- A continuous Fourier Transform Infra-red (FTIR) spectrometer (Protea, ProtIR 204 M) for the quantification of CH_3NH_2 , NH_3 , HCN, NO, NO_2 and CO_2 , mainly.

As it can be seen, this configuration allows the quantification of numerous species, some of them in duplicate, which contributes to the reliability of the results obtained experimentally. The uncertainty of the measurements is estimated within $\pm 5\%$, but not less than 5 ppm for the continuous analyzer and the FTIR spectrometer, and not less than 10 ppm for the gas micro-chromatograph. An example of comparison of this double quantification is shown in Fig. 1. For greater clarity, the results corresponding to NH_3 and HCN have been colored.

For a deeper analysis of the pyrolysis and oxidation of methylamine, in the absence and presence of NO, the present experimental conditions have been simulated, and the results interpreted, using the chemical kinetic mechanism developed by Glarborg et al. [29] (including thermodynamic data). Modeling calculations have been performed with the plug-flow reactor module of the software Chemkin-Pro software package [32].

3. Results and discussion

3.1. Methylamine oxidation in the absence of NO

Fig. 2 shows a comparison of experimental results and model predictions for the oxidation of CH_3NH_2 at stoichiometric conditions as a function of temperature. In addition to the consumption

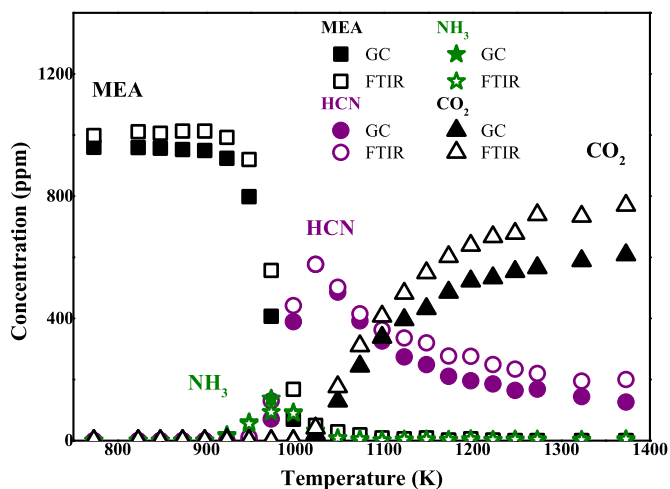


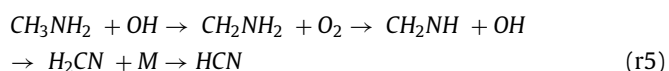
Fig. 1. Comparison of experimental measurements for MEA consumption and NH_3 , HCN and CO_2 formation with different equipment: gas micro-chromatograph (GC) and Fourier Transform Infra-red (FTIR).

of the reactants, MEA and O_2 , the formation of the different products can be observed. From now on, symbols denote experimental data, while solid lines denote model predictions.

Methylamine oxidation starts at around 925 K and at 1025 K it is almost fully converted to HCN, but also NH_3 and nitrogen oxides, namely NO and N_2O , are formed. In general, there is a good agreement between experimental data and modeling calculations. The largest discrepancies are found in the case of NH_3 and NO, whose concentrations are underestimated and overestimated, respectively, which is why NH_3 results have been highlighted in blue in Fig. 2.

Experiments for stoichiometric conditions in the absence of NO have been carried out in duplicate to assess the accuracy of the measurements, they correspond to sets denoted as 3 and 4 in Table 1. Thus, for each temperature point studied within the whole range considered in this study, two results are obtained. Fig. 3 shows a comparison of concentration results obtained in both cases for methylamine (MEA) consumption, and CO_2 and HCN formation, as two of the major products. The experimental error has been estimated by calculating the pooled standard deviation (i.e., the square root of the sum of squares of the error) associated with the MEA normalized concentration. It has been done in this way because the MEA concentration has not been always the same fed to the reaction system. In this way, the pooled standard deviation obtained is 0.03, i.e., around 3%, considering that the experimental error does not depend on the temperature within the temperature range considered.

Under the present conditions, the methylamine consumption routes are equal to those previously described by Glarborg et al. [29]. They developed a mechanism based on few flow-reactor experimental data (mainly products quantification) from literature works. In those works, oxidation of CH_3NH_2 was studied under significant oxygen excess conditions, both in the absence and presence of NO [24,25]. They can be summarized in the following reaction sequence (r5):



Methylamine is mainly consumed by H-abstraction reactions from the carbon site. The other possible abstraction site, the nitrogen site, to form CH_3NH has less relevance in the oxidation process.

The influence of the oxygen availability in the reactant mixture has been evaluated through the variation of the air excess ratio

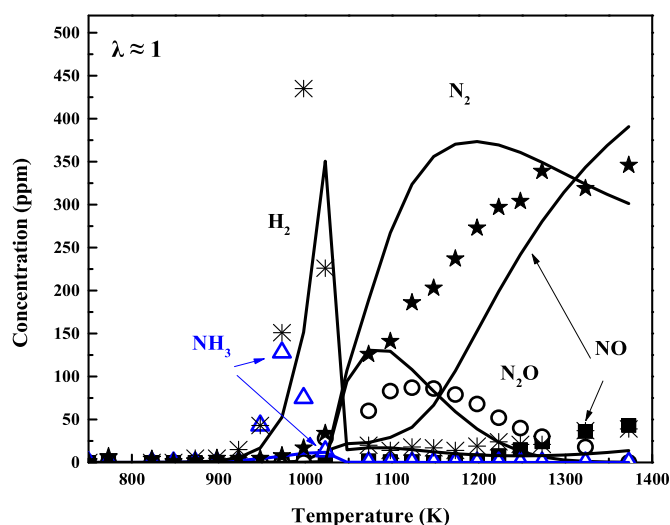
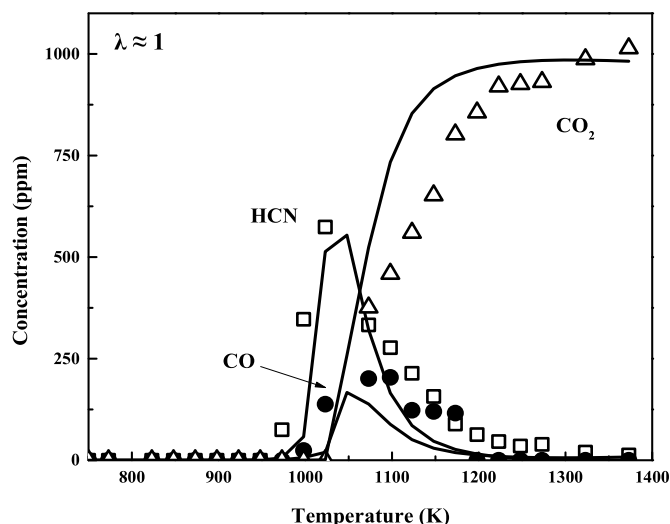
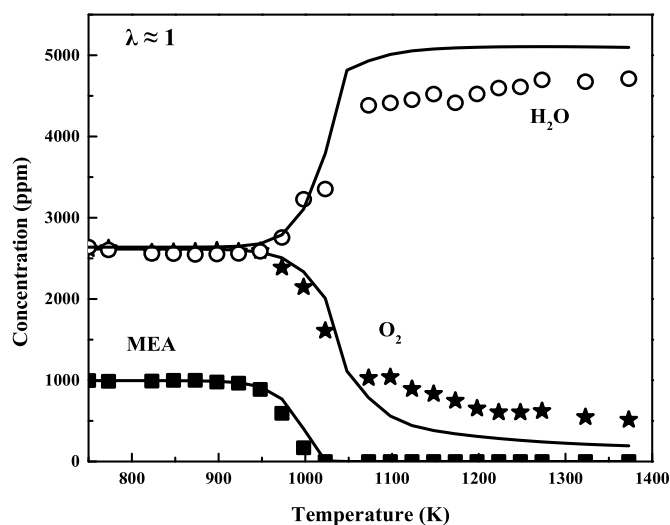


Fig. 2. Comparison of experimental results and model calculations for CH_3NH_2 oxidation and products formation in a flow reactor at stoichiometric conditions. Experimental conditions correspond to set 4 in Table 1.

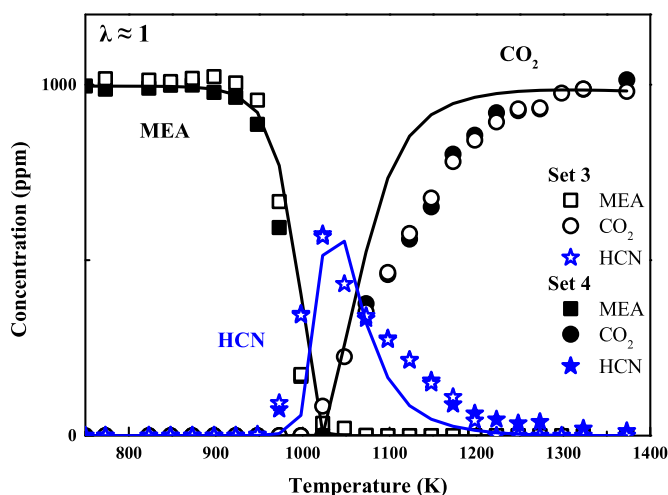


Fig. 3. Repeatability study: comparison of concentration results for MEA as a reactant and CO₂ and HCN as products for the conditions denoted as sets 3 and 4 in Table 1.

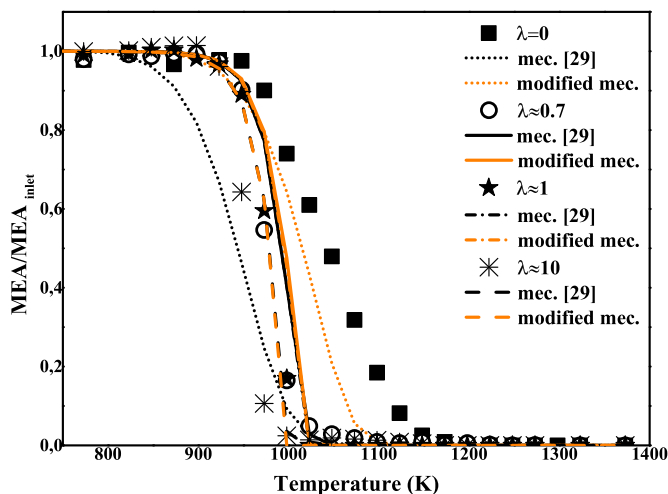


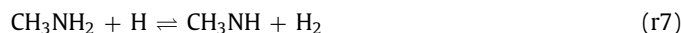
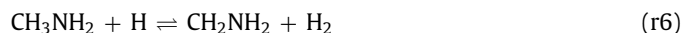
Fig. 4. Influence of the air excess ratio (λ) on the concentration profile of MEA as a function of temperature for the atmospheric oxidation of MEA in a flow reactor. (Sets 1, 2, 4 and 5 of Table 1).

(λ) from pyrolysis ($\lambda = 0$) to fuel lean-conditions ($\lambda \approx 10$). Both experimental and modeling results for the consumption of MEA are shown in Fig. 4. For a better comparison of the results, the MEA concentration has been normalized with respect to its inlet concentration (approximately, 1000 ppm). The experimental results for the rest of the quantified species are shown in Figures S1-S5 in the Supplementary Material.

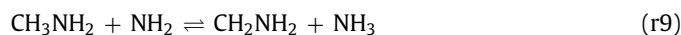
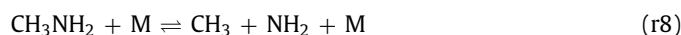
As it can be seen, MEA consumption barely follows the same pattern regardless of oxygen availability. It starts at around 925 K for $\lambda \approx 0.7, 1$ and 10, and only for fuel-lean conditions, at the same temperature a higher conversion is achieved. However, under pyrolysis conditions, MEA consumption starts at higher temperatures. Under these circumstances, the largest discrepancy between experimental results and modeling calculations has been found, with the model predicting an onset of MEA conversion at temperatures even lower than for fuel-lean conditions. As reported by Glarborg et al. [29], their model was not evaluated against pyrolysis data from earlier literature studies from batch reactors [18] and shock tubes [33–35].

In order to further analyze the reason for the discrepancies observed, a reaction rate analysis for pyrolysis conditions was performed. Results indicate that the main consumption of methyl-

amine is through H-abstraction reactions by H radicals (reactions r6 and r7). As previously indicated during the oxidation reaction pathways analysis, there are two possible abstraction sites, with the carbon site being the preferred (reaction r6) as reported by Glarborg et al. [29] based on the theoretical work by Kerkeni and Clary [36] and coinciding with the early observations of Emel us and Jolley [18] and Cullis and Willsher [20].



In the initial steps of methylamine conversion, H radicals are generated as follows. First, methylamine dissociates thermally by breaking the C–N bond, reaction (r8). Second, the generated amino radicals interact with methylamine, removing an H atom from the carbon and forming ammonia and the CH₂NH₂ radical, reaction (r9), which thermally dissociates, releasing the active H radicals, reaction (r10).



Therefore, based on this analysis, reaction (r10) seems to play a crucial role in predicting an onset of MEA conversion about 100 K less than experimentally detected. The chemical kinetic parameters included in the initial mechanism [29], Table 2, were taken from the work of Dean and Bozzelli [37] and correspond to a theoretical determination in a N₂ atmosphere based on a QRRK analysis. An attempt for a better agreement between experimental and modeling results has been performed by including new kinetic parameters for reaction (r10). Specifically, the parameters proposed by Deppe et al. [38] (Table 2), for the thermal decomposition of NH₂ radicals, reaction (r11), by analogy with reaction (r10), have been included.



Deppe et al. [38] measured the rate constant and product channels for the decomposition of NH₂ behind shock waves and monitoring the NH₂ concentration by laser adsorption and frequency-modulated (FM) spectroscopy, the concentration of NH by laser adsorption and H and N atoms were followed by means of ARAS. Results suggest a reaction rate for the unimolecular decomposition of NH₂ into NH as shown in Table 2.

Additionally, Figure S6 shows a comparison of the calculated values of the rate constants for reaction (r10) for the 500–2000 K temperature range, which illustrates the difference between the kinetic parameters proposed in the work of Dean and Bozzelli [37] and the ones taken by analogy from Deppe et al. [38].

Fig. 4 includes modeling predictions also with the kinetic parameters of Deppe et al. [38] (denoted by orange short dot lines). As it can be observed, the modified mechanism is closer to experimental data under pyrolysis conditions, hardly modifying the previous results for the rest of the air excess ratios studied (black and orange lines are overlapped). Figures S1-S5 in Supplementary Material corresponding to the other quantified species, as previously mentioned, also shows a comparison of modeling results using the Glarborg et al.'s mechanism [29] and the one modified in the present work with also an improvement in the agreement between experimental and modeling results for pyrolysis conditions.

Table 2
Kinetic parameters for the modified Arrhenius expression.

reaction	A	n	Ea	Source
$\text{CH}_2\text{NH}_2 \rightleftharpoons \text{CH}_2\text{NH} + \text{H}$	$2.4 \cdot 10^{48}$	-10.82	52,040	Dean and Bozzelli [37]
$\text{NH}_2 \rightleftharpoons \text{NH} + \text{H}$	$1.99 \cdot 10^9$	0.0	76,000	Deppe et al. [38]

^aUnits are mol, cm, s, cal.

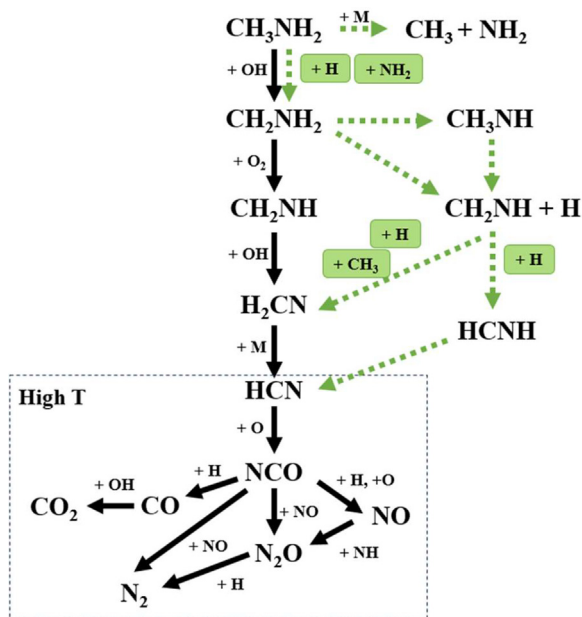


Fig. 5. Main reaction pathways for methylamine consumption under fuel-lean (black lines) and pyrolysis conditions (dotted green lines).

The worst agreement between experimental and modeling calculations is obtained in the case of NH_3 . However, under pyrolysis conditions, with the modification made to the kinetic mechanism, the agreement has improved until temperatures around 1100 K, which correspond to the temperature range where the maximum NH_3 concentration is achieved.

Fig. 5 summarizes and compares the main methylamine consumption routes under fuel-lean and pyrolysis conditions obtained with the Glarborg et al.'s mechanism slightly modified in the present work.

According to the reaction pathways summarized in **Fig. 5**, there are several paths that involve NO and N_2 in the high temperature range. They can help to explain the over-prediction of NO by the model, especially relevant for fuel-lean conditions (Figure S5). It may be related with the under-prediction of N_2 , as can be seen in the right side of Figure S3, where a higher N_2 concentration than predicted by the model is detected experimentally.

3.2. Methylamine oxidation in the presence of NO

The influence of the presence of NO in the reactant mixture has been evaluated for stoichiometric conditions: two different NO inlet concentrations have been tested, around 500 and 1000 ppm. A comparison of the experimental and modeling is shown in **Fig. 6** for MEA and NO consumption. The formation of N_2 and HCN as the main nitrogen products is also shown. Modeling calculation have been performed with the mechanism modified in the present work.

The presence of NO significantly promotes MEA conversion, shifting the onset for MEA consumption to lower temperatures, regardless of the inlet NO concentration. This increased reactivity at low temperatures can be explained by the involvement of NO in

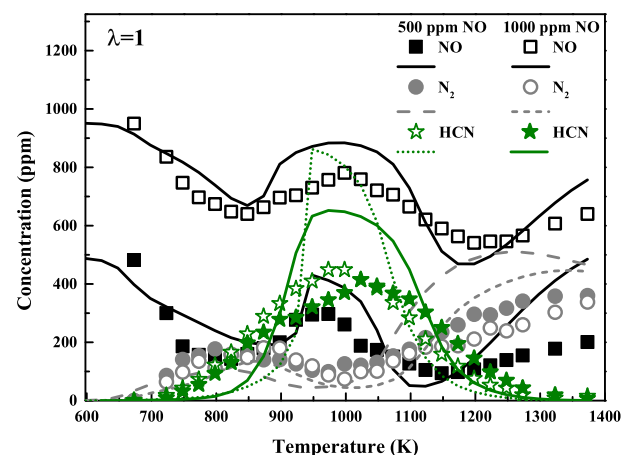
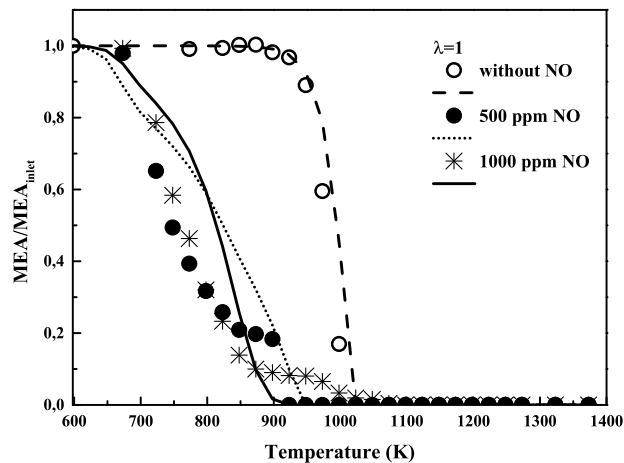
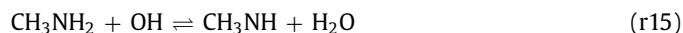
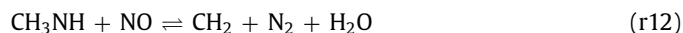
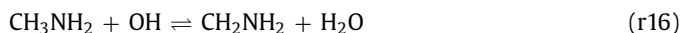


Fig. 6. Influence of the presence of NO (500 or 1000 ppm) in MEA consumption for stoichiometric conditions (top). NO, N_2 and HCN concentration profiles as a function of temperature during the MEA oxidation in the presence of NO (bottom). Experiments 4, 6 and 7 of **Table 1**.

the reaction (r12), and because NO participates in a reaction cycle forming NO_2 , which is recycled back to NO, accompanied by the release of highly reactive hydroxyl radicals (reactions r13 and r14). It implies an increased relevance of the H-abstraction reaction from the amino group of methylamine by hydroxyl radicals, reaction (r15), not relevant in the absence of NO as mentioned above. Consequently, at low temperatures, the NO concentration decreases by increasing the N_2 concentration.



As indicated above, the carbon site is preferred for the H-abstraction from methylamine, in the presence of NO by hydroxyl radicals, i.e. reaction (r16) dominates over reaction (r15).



At intermediate temperatures (around 950 K), CH_3NH is mainly consumed by reaction (r17), increasing the formation of HCN, see reaction sequence (r5), but decreasing the consumption of NO.



Finally, at higher temperatures, around 1200 K, methylamine consumption through thermal decomposition breaking the C–N bond becomes more relevant, reaction (r8), and the increase in the N_2 concentration can be explained by reaction (r18).



The NO–NO₂ reaction cycle mentioned above (reactions r13 and r14) is present under all the temperature range considered. Experimentally, no formation of NO₂ in appreciable quantities has been detected.

4. Conclusions

During the oxidation of methylamine, from pyrolysis to fuel-lean conditions, a large number of different products has been quantified. In addition, this work provides experimental data at stoichiometric conditions that allow the analysis of the effect of the presence of NO since, until this moment, this had only been addressed from a theoretical/modeling perspective or under highly fuel-lean conditions. The experimental results of this research contribute to the development, validation, and refinement of detailed chemical kinetic mechanisms.

The oxygen availability (different air excess ratios, from pyrolysis to significantly fuel lean conditions, have been tested) has almost no effect on the oxidation of methylamine. However, the presence of NO in the reactant mixtures promotes MEA oxidation at lower temperatures, independently of the NO inlet concentration.

The comparison of the present experimental results with modeling calculations using a literature mechanism exhibits reasonably good results, but also indicates that there is still room for improvement, especially for pyrolysis conditions and the formation of NH₃ and NO as oxidation products, where the largest discrepancies have been found in this work.

Novelty and significance statement

New well-controlled methylamine oxidation experiments have been performed in a quartz flow reactor covering a wide range of temperatures and air excess ratios (from pyrolysis to fuel-lean conditions). For the first time, the influence of NO addition (500 and 1000 ppm) on the stoichiometric oxidation of methylamine has also been experimentally evaluated, and the main products of such interaction have been identified.

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.

CRediT authorship contribution statement

Lorena Marrodán: Conceptualization, Methodology, Formal analysis, Investigation, Writing – review & editing, Supervision. **Teresa Pérez:** Methodology, Formal analysis. **María U. Alzueta:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2023.113130.

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