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High-pressure study of the conversion of NH_3/H_2 mixtures in a flow reactor

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ABSTRACT

Carbon free fuels such as hydrogen (H_2) and ammonia (NH_3) will probably play a fundamental role owing to their potential for clean combustion without CO_2 emissions. To contribute to the knowledge and development of technologies based on carbon free combustion, the present work deals with an experimental and kinetic analysis of ammonia oxidation in its mixtures with hydrogen at high pressure (up to 40 bar), in the 250–1250 K temperature range using a quartz tubular reactor and argon as bath gas. The impact of temperature, pressure, stoichiometry and H_2/NH_3 ratio on the concentrations of NH_3, NO, NO_2, N_2O, and N_2 obtained as main products of oxidation has been analyzed. The main results indicate that either increasing pressure, H_2/NH_3 ratio or oxygen availability results in a shift of NH_3 and H_2 conversion to lower temperatures. The NH_3 and H_2 consumptions are promoted by the reactions that produce NH_2, H, OH, O, HO_2 and HNO species and inhibited by reactions that form H_2O, NH_3, NO, H_2NO and O_2 species. The pressure effect is particularly significant in the low range of pressures studied. The main ammonia oxidation nitrogen products are N_2 and N_2O, while NO and NO_2 concentrations are below the detection limit under all considered conditions. N_2O formation is favored by increasing stoichiometry, pressure and H_2/NH_3 ratio. The experimental results are simulated and interpreted in terms of a literature detailed chemical kinetic mechanism, which, in general, is able to describe quite well both the H_2 and NH_3 conversion profiles under the studied conditions.

1. Introduction

Net-zero emission fuel use is expected to grow by 2050. Hydrogen is projected to account for 28% of the transport energy required for that date [1]. In this context, fuels such as H_2 and NH_3 play a critical role due to their potential for clean combustion without CO_2 emissions, and H_2O and N_2 as reaction products, through $4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$ (R1) [2] and $2H_2 + O_2 \rightleftharpoons 2H_2O$ (R2). The advantages of using NH_3 in power generation turbine systems [3] or combustion engines include established manufacture, safe transport, storage and developed infrastructures [4–6]. The use of NH_3 as a fuel also presents some drawbacks such as low heating value and flame speed [7], and high autoignition temperature [8] than other hydrocarbon fuels, together with the possible NO_x and unburned NH_3 emissions [4,9]. In this sense, a possible solution to palliate these barriers and improve NH_3 combustion characteristics is to mix it with other fuels: e.g. H_2 [6,10–17], CH_4 [3,7,18–20] and DME [21–23]. Despite the fact that the CH_4 and DME addition improves the combustion properties of ammonia mixtures, some CO_2 is still emitted. In this line, NH_3/H_2 mixtures have a special interest because H_2 is the most effective additive to enhance the NH_3 burning velocity [24] and the cleanest of previously mentioned fuels in terms of carbon emissions. At the same time, mixing NH_3 and H_2 improves the safety of H_2 combustion [13,14]. In general, the addition of H_2 to the fuel mixture, even in small fractions, enhances the ignition of NH_3, as has been reported even for small amounts of H_2 to the fuel mixture, such as 5 % [1,16]. This enhancement is attributed to the increase in H, O and OH radicals produced by adding H_2 to the mixture. This is consistent with the fact that the reaction $NH_3 + OH \rightleftarrows NH_2 + H_2O$ (R3) appears as an important NH_3 consumption reaction particularly when H_2 is added [12]. Alturaifi et al. [12] identified some important equations that cause this increase in H-radicals such as $NH_2 + H_2 \rightleftarrows NH_3 + H$ (-R4). Additionally, the use of NH_3/H_2 blends avoids the production of HCN and has a lower NO production potential [25] than the mixture with hydrocarbons. However, compared with pure NH_3 and pure H_2 combustion, the NH_3/H_2 combustion increases NO_x and unburn NH_3 emissions during combustion [1], and this is one of the most noticeable challenges for NH_3/H_2 implementation as an energy source. At this point, it is important to note that working at high pressures can result in lower NO emissions [25]. In the meantime, further work is needed to develop and test a reaction kinetic mechanism to understand better the

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chemistry of NH_3 in its combustion with H_2, since there are discrepancies in the most accurate models provided in the literature [12], and this is one of the aims of this work. In the recent literature, a number of experimental and kinetic works on NH_3/H_2 mixtures combustion at low pressure (from 0.05 to 5 bar), performed using different experimental set-ups, can be found, although only two of them in flow reactors to our knowledge. It should be noted that most of the works in the literature are focused on flame studies including stability, flame structure, laminar burning velocity, ignition delay times and NO_x formation. Nevertheless, there is a gap in knowledge regarding studies performed using plug-flow reactors. From an industrial application point of view, it is important to mention the works carried out at pressures over 5 bar are still scarce. Studies at high pressure available include works in a rapid compression machine (RCM) [16,26,27], a swirl burner [28], a combustion tube [29] and a cylindrical combustor [30]. It can also be mentioned the numerical study of Li et al. [31] that focused on NO_x emissions characteristics at high-pressure. Dai et al. [16] determined ignition delay times of the NH_3/H_2 oxidation for different H_2 fractions (5% and 10%) at 20 and 60 bar from reducing to oxidizing conditions ($\lambda = 0.33$, 0.5, 1 and 2) in a RCM and elevated temperature from 1040 K to 1210 K. He et al. [26] studied the autoignition properties and species concentration of NH_3/H_2 oxidation in argon at 20 and 60 bar from $\lambda = 0.67$ to $\lambda = 2$ in a RCM and elevated temperature from 950 K to 1150 K. Pochet et al. [27] studied the influence of H_2 addition to NH_3 on ignition delay times at 43.4 and 65.5 bar at $\lambda = 2$ and $\lambda = 5$ in a RCM and temperatures from 1000 K to 1100 K. Valera-Medina et al. [28], Li et al. [29] and Mei et al. [30] performed the other high-pressure experimental and numerical works mentioned above, up to 10 bar, in which NO_x formation, species concentration, flame morphology, laminar burning velocities were determined. Increasing the pressure can reduce the unburned NH_3 and NO production [17,25]. However, the effect on N_2O formation is not so clear and results by Wang et al. [25] in a pressure study, up to 5 bar, have shown different trends compared to results obtained in the oxidation of NH_3/CH_4 mixtures [32]. So, N_2O production at high pressures deserves further study, as considered in the present work.

In this scenario, the objective of this work is to provide new experimental data on the combustion of NH_3/H_2 mixtures in a high pressure and temperature quart flow reactor setup, analyzing the effect as main variables of temperature, pressure, oxygen excess and H_2/NH_3 ratios. Experimental results are interpreted in terms of a chemical kinetic mechanism taken from previous work [32], to understand the chemistry and product formation, and to determine the main reaction pathways through which reactions proceed.

2. Methodology

Conversion of reactants and formed products during the combustion of a NH_3/H_2 mixture are studied at high pressure (10, 20, 30 and 40 bar) in a well-controlled laboratory-scale quartz flow reactor setup. Additionally, to pressure, other variables considered include stoichiometry (stoichiometric, $\lambda = 1$, and oxidizing, $\lambda = 3$, conditions), and the H_2/NH_3 ratio (0.5, 1 and 2) which means using H_2 nominal concentrations of 500 ppm, 1000 ppm and 2000 ppm for an NH_3 nominal concentration of 1000 ppm in a wide range of temperatures (from 250 K to 1250 K). The experimental set-up has been used in success and described in previous works e.g. [32–35]. The oxygen excess ratio (λ) is defined on the basis of the NH_3 oxidation reaction to N_2 (R1):

$$\lambda = [O_2]_{inlet}/[O_2]_{stoichiometric}, \quad (1)$$

and the flow rate is 1 L(STP)/min, and implies a temperature and pressure dependent gas residence time in the isothermal reaction zone:

$$t_r\ (s) = 231.6 \cdot P(bar)/T(K), \quad (2)$$

where P and T are the gas pressure and temperature. Experiments are performed using argon as a bath gas, which allows us to determine the molecular nitrogen formed during reaction, and to calculate the nitrogen atoms balance. In the experiments, H_2, O_2, and N_2 concentrations are analyzed and quantified with a gas micro-chromatograph (Agilent Technologies) and a $NH_3/NO/NO_2/N_2O$ continuous analyzer (ABB, model: Advance Optima AO2020). The estimated measurement uncertainty is $\pm$ 5 %, but not less than 5 ppm for the continuous analyzer and 10 ppm for the gas micro-chromatograph. Table 1 summarizes the experimental initial conditions. Sets 5 and 5R correspond to similar experiments to evaluate repetitiveness.

The experimental results have been analyzed using a gas-phase chemical kinetic mechanism, to describe the oxidation of NH_3/CH_4 under high-pressure conditions, without modification [32]. Fig. S1 of the supplementary material shows an example of the validation of the present mechanism against literature data [36] for a plug flow reactor under atmospheric conditions. Calculations have been carried out using the plug-flow reactor (PFR) model of the Chemkin Pro suite [37], using the initial conditions for each experiment, as listed in Table 1, and a "fix gas temperature" type problem, using the nominal reaction temperature at the flat temperature zone, since similar results were obtained with and without the measured temperature profiles.

3. Results

3.1. Effect of pressure

Fig. 1 and 2 show the conversion of NH_3 and H_2 respectively as a function of temperature for different pressures (from 10 to 40 bar), H_2/NH_3 ratios (0.5, 1 and 2), and oxygen excess ratios (λ = 1 and 3). Keeping the rest of the conditions similar, each increase of pressure of 10 bar (from 10 to 40 bar) makes the NH_3 conversion onset for $\lambda = 1$ to vary to lower temperatures, following the sequence 50 K, 50 K and 15 K (temperatures of respectively 925 K, 875 K, 825 K and 810 K) for H_2/NH_3 = 1; Similarly, under oxidizing conditions (λ = 3) the shift in temperature values is 50 K, 25 K and 25 K (925 K → 875 K → 850 K → 825 K) for $H_2/NH_3 = 0.5$. For $H_2/NH_3 = 1$, the reduction is 50 K, 25 K and 0 K (875 K → 825 K → 800 K → 800 K) and for the higher H_2/NH_3 ratio studied is 25 K, 25 K, 0 K (850 K → 825 K → 800 K → 800 K). Similar observations can be done for the onset temperature of the H_2 oxidation reaction and for each pressure increase under the same conditions. As can be seen, the reaction onset temperature of NH_3 oxidation when mixed with H_2 shows a pressure dependence, as pointed out by other authors [16,26]. He et al. [26] reported that increasing the pressure results in an increase in reactivity and a decrease in the ignition delay time by a factor of 10 using a RCM system in the 20–40 bar range and 5 % of H_2 in the mixture. Generally, the onset temperature decreases with increasing pressure at all conditions studied, as also observed with

Table 1
Matrix of mixture compositions in the present work. (Concentrations in ppm).

Set	NH_3	H_2	O_2	P (bar)	λ
1	1092	421	2933	10	2.85
2	1064	422	2906	20	2.89
3	1067	424	3036	30	3.00
4	848	432	2866	40	3.35
5	1084	914	1234	10	0.97
5R	1092	873	1239	10	0.99
6	1081	814	1197	20	0.98
7	1038	972	1184	30	0.94
8	1102	879	1212	40	0.96
9	1107	899	3857	10	3.01
10	1096	867	3746	20	2.98
11	1027	936	3658	30	2.95
12	1059	891	3602	40	2.91
13	885	1851	5135	10	3.23
14	874	1854	5197	20	3.28
15	882	1899	5133	30	3.19
16	858	1806	5113	40	3.31

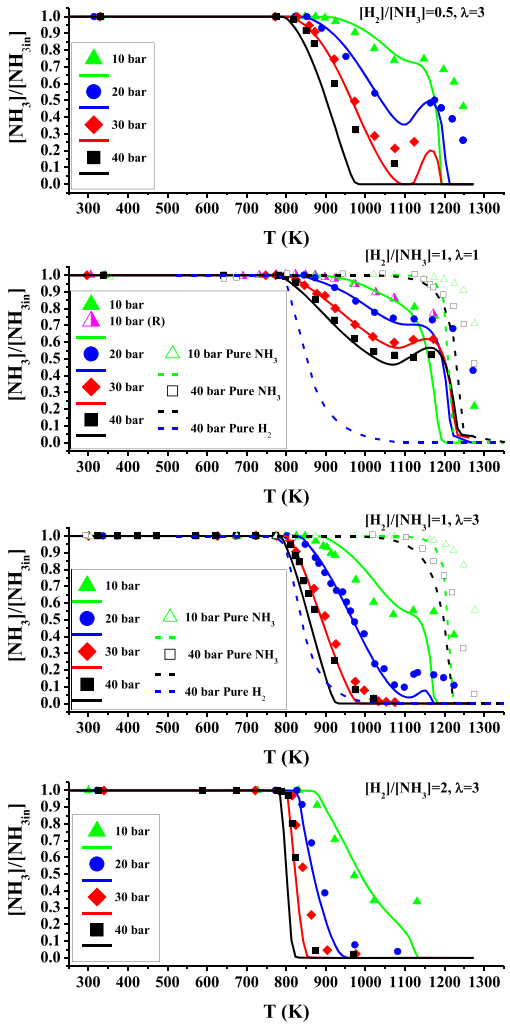

Fig. 1. NH_3 conversion as a function of temperature for different pressures (10–40 bar), sets 1–16 in Table 1.

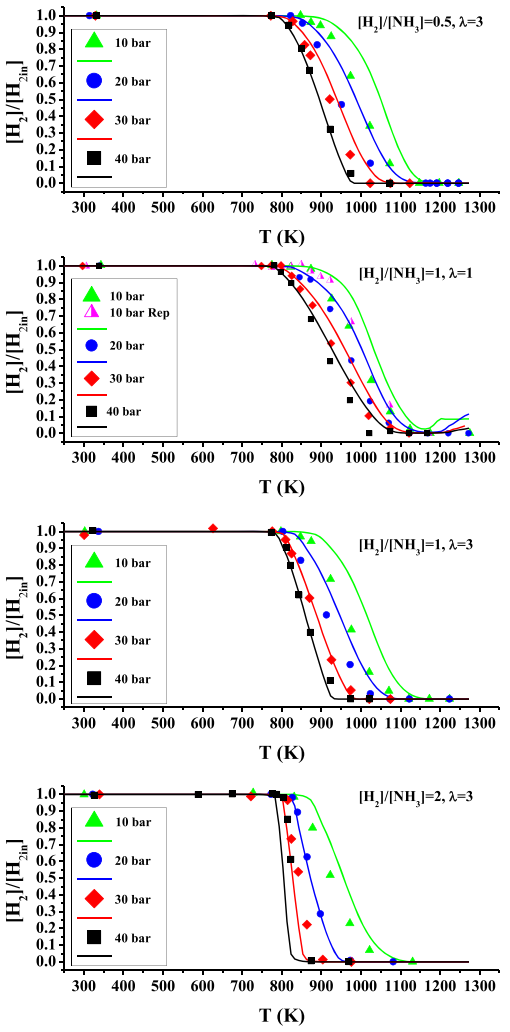

Fig. 2. H_2 conversion as a function of temperature for different pressures (10–40 bar), sets 1–16 in Table 1.

pure NH_3 oxidation at high pressure [34]. In Fig. 1 and 2 it should be noted that the effect of pressure on the NH_3 and H_2 reaction onset temperature is slightly minor as the H_2/NH_3 ratio increases, under the studied conditions. The same trend in reaction onset temperature for NH_3 and H_2 oxidation can be seen with increasing excess oxygen from stoichiometric ($\lambda = 1$) to oxidizing conditions ($\lambda = 3$), for $H_2/NH_3 = 1$. Nevertheless, for NH_3 oxidation, the pressure has a significant effect on the unburned NH_3. It can be observed that the conversion of NH_3 is much higher at higher pressures at intermediate and high temperatures. This is not the case for H_2 oxidation, which achieves complete conversion under all studied conditions. The pressure effect is also found in the case of oxidation of pure NH_3 [34], although less important than for the H_2/NH_3 mixture. For pure NH_3, at 10 bar, unburned NH_3 is found at high temperatures (1250–1300 K), while at 40 bar, there is no unburned NH_3 under oxidizing conditions at 1275 K. The effect of H_2 addition on the NH_3 ignition is noticeable, as the NH_3 reaction onset temperature decreases 250 K-350 K for the studied conditions when compared to pure NH_3 [17,34], in agreement with other authors findings [1,12,16]. Apart from pressure, the oxygen availability logically has a remarkable effect in the unburned NH_3, which is much larger at $H_2/NH_3 = 1$ and $\lambda = 1$ than in the rest of the conditions for $\lambda = 3$, even in the case of $H_2/NH_3 = 0.5$, in the line with the results of Osipova et al. [17] in a jet stirred reactor at atmospheric pressure.

In general, the model reproduces quite well the reaction onset temperature and the main trends of NH_3 and H_2 consumption, for the different pressures at $\lambda = 1$ and 3 conditions of Fig. 1 and 2. The model shows that the main NH_3 consumption pathways are $NH_3 \rightarrow NH_2 \rightarrow N_2$ and $NH_3 \rightarrow NH_2 \rightarrow H_2NO \rightarrow HNO/HONO \rightarrow NO \rightarrow NO_2 \rightarrow N_2O$. The consumption pathway of H_2 is $H_2 \rightarrow H \rightarrow HO_2 \rightarrow OH \rightarrow H_2O$ (Fig. S2-S5). The autoignition enhancement of ammonia occurs due to the increase in H, O and OH radicals by the addition of H_2 [1,12]. This increase in the H/O radical pool leads to a higher consumption of NH_3 and NH_2. The model is also able to reproduce the decrease of NH_3 consumption produced at 900 K-1100 K as can be observed in Fig. 1 in the three first cases ($H_2/NH_3 = 0.5$ and 1). The main NH_3 consumption reaction is $NH_3 + OH \rightleftharpoons NH_2 + H_2O$ (R3) and the two main NH_3 production reactions are $NH_2 + H_2 \rightleftarrows NH_3 + H$ (-R4) and $H_2NO + NH_2 \rightleftharpoons HNO + NH_3$ (R5), when 10 % of NH_3 is consumed (Fig. S2-S5). H_2 is consumed by $NH_2 + H_2 \rightleftarrows NH_3 + H$ (-R4) and $OH + H_2 \rightleftharpoons H + H_2O$ (R6), under the same conditions (Fig. S2-S5). NH_3 and H_2 consumption is promoted by reactions (-R4) and (R6) while (R3) and (R5) imply inhibition effects (Fig. S6-S9). When H_2 is added, the concentration of the O/H radical pool is increased by chain branching reactions. The H_2 consumption reactions provoke the increase in H radical via (-R4) and (R6), which is consumed mainly by its reaction with NO_2 and O_2 producing OH: $NO_2 + H \rightleftharpoons NO + OH$ (R7), and HO_2: $H + O_2 (+M) \rightleftharpoons HO_2 (+M)$ (R8) respectively. The HO_2, produced by (R8) and $HNO + O_2 \rightleftharpoons HO_2 + NO$ (R9), leads to the formation of OH by reaction with NO: $HO_2 + NO \rightleftharpoons NO_2 + OH$ (R10). In addition to this reaction, $HONO (+M) \rightleftharpoons NO + OH (+M)$ (-R11) also contributes to OH formation (Fig. S2-S5). To a minor extent, O radicals are formed by the

reaction H + O_2 ⇌ O + OH (R12), which efficiently promotes NH_3 and H_2 conversion, and are consumed forming OH and H radicals. OH radicals are then consumed by (R3) and (R6) (Fig. S2-S5). Reaction (R7) has an inhibitory effect on NH_3 and H_2 consumption under all studied conditions, while (R8) only under the lowest pressure studied, showing a pressure dependence (Fig. S6-S9). However, in the 900–1200 K range, the H_2 is depleted and the rate of OH radical production decreases due to the decrease in H radicals following the same trend as NH_3 consumption. In the decrease of the O/H radical pool, the species NO, NO_2, HNO, H_2NO, HONO, H, HO_2, and O are involved. In more detail, in temperatures lower than the one of the "NTC" behavior, the produced H radicals are consumed mainly by the reaction NO_2 + H ⇌ NO + OH that produces OH radicals and to more extent by reaction H + O_2 (+M) ⇌ HO_2 (+M) that contributed to OH formation through HO_2 + NO ⇌ NO_2 + OH reaction, as mentioned before. These reactions represent the main source of OH radicals. However, in the "NTC" area, the reaction rate of these H consumption reactions decreased by one order of magnitude, and this decrease in the reactions forming OH radical provokes the reduction in the NH_3 consumption.

When H_2 is fully consumed before the NH_3 is depleted, the rate of NH_3 consumption decreases due to the decrease in OH radicals, and thus a saddle point is produced and, in some cases, even a small increase in the NH_3 concentration in the reactor outlet at the highest temperatures studied (950 K–1250 K), similar to the NTC behavior of oxygenated fuels. The reason why this is not seen at the higher pressures studied is owing to the fact that NH_3 and H_2 are completely burned at the same temperature. Osipova et al. [17] reported that the O/H radical pool starts to form at lower temperatures in the presence of H_2 under atmospheric pressure conditions. It appears that at high pressure this effect also occurs, and is responsible for the decrease in the onset temperature of the NH_3 conversion compared to the pure NH_3 oxidation for similar conditions.

Fig. 1 and 2 also show the repeatability of sets 5 and 5R. As can be seen, the reproducibility of the experiments is quite good over the whole temperature range considered, which indicates that the experimental system and the experimental procedure are performing adequately. Fig. S2 to S9 of the Supplementary material (SM) include the reaction path diagrams and sensitivity analysis for NH_3 and H_2 consumption for the studied conditions under the highest (40 bar) and lowest (10 bar) studied pressures, when 10 % of the NH_3 is consumed in any case. Fig. S10 of the supplementary material includes a comparison between the oxidation of NH_3, NH_3/H_2 and NH_3/CH_4 mixtures.

3.2. Effect of stoichiometry (λ) and composition (H_2/NH_3 ratio)

Experimental results show a clear sensitivity to oxygen availability, which has an important effect on NH_3 consumption and emissions. First, because oxygen is involved in OH radical production and second, because is involved in NH_3 and H_2 promoting reactions. NH_3 and H_2 conversion starts at a lower temperature at λ = 3, and, where possible, NH_3 is consumed under oxidizing conditions, Fig. 1 and 2. This is in line with the findings of Dai et al. [16] and Osipova et al. [17], who found that the autoignition of NH_3/H_2 mixtures is enhanced by increasing the oxygen excess ratio. The oxygen availability effect is more pronounced in the mixture than for pure NH_3 [34], under similar experimental conditions.

Increasing the H_2/NH_3 ratio also improves the combustion characteristics of NH_3 due to the increase in H radicals and, consequently the OH radicals through H + O_2 ⇌ O + OH (R12). Under oxidizing conditions and 40 bar, pure NH_3 starts to convert at 1125 K [34] while when mixed with H_2, conversion occurs at 300 K less, (800–825 K for H_2/NH_3 = 0.5, 1 and 2). For similar conditions, the H_2/NH_3 mixtures also start to convert at lower temperatures than CH_4/NH_3 mixtures, where the NH_3 reaction onset temperature is 875 K, 825 K, and 825 K for 40 bar and CH_4/NH_3 = 0.5, 1 and 2 respectively [32]. The oxygen excess ratio and H_2/NH_3 ratio also affect N_2O production, which is discussed in the next section.

3.3. NO, NO_2 and N_2O emissions

Fig. 3 shows the N_2O formation peak as a function of temperature. The maximum concentration of N_2O is achieved between 975 and 1025 K in all cases except for the H_2/NH_3 = 2 ratio in which it was located between 875 and 1025 K (Fig. S11). However, no significant concentrations of NO or NO_2 were found at the reactor output (Fig. S12 and S13).

The NO_2 formed is quickly consumed through NO_2 + H_2NO ⇌ HONO + HNO (R16) (more accentuated at lower pressures), or NO_2 + H ⇌ NO + OH (R17) particularly as pressure increases, and especially through its reactions with NH_2 to generate H_2NO + NO (R18) and N_2O + H_2O (R19), the latter responsible for N_2O formation. N_2O consumption occurs mainly through decomposition as the temperature is high enough: N_2O (+*M*) ⇌ N_2 + O (+*M*) (R20) (Fig. S2-S5).

As can be observed in Fig. 3, the formation of N_2O is favored by pressure. N_2O maximum peak is 7 times higher at 40 bar than at 10 bar in the case of 500 ppm H_2, contrary to what Wang et al. [25] reported for low pressures (from 1 to 5 bar). For the same H_2 fraction (H_2/NH_3 = 1), at λ = 3, the N_2O formation peak is 2 to 4 times higher than for λ = 1, under 40 to 10 bar respectively. Thus, the H_2/NH_3 ratio is an influential variable for ta given oxygen availability, since an increase in H_2 leads to an increase of N_2O formation for each pressure studied by a factor of 1.5–2. These results contrast with those found for the oxidation of pure NH_3, where no N_2O emissions were found in the same experimental set-up, and similar temperatures and pressures [34].

In the oxidation of NH_3 mixtures with CH_4 [32], a N_2O maximum peaks of 140 ppm, 100 ppm, 215 ppm and 290 ppm were respectively reached for the same studied conditions as with H_2 in the present work, which indicates a consistency of the results. It can be seen that although the N_2O peak formation under the present conditions follows the same trend as in previous work [32], the amount of N_2O formed is lower in the H_2 mixture compared to the CH_4 one. Thus, working with higher oxygen excess ratios than 1 is desirable to reduce the unburned NH_3 despite the higher N_2O production, which is the main drawback of NH_3/H_2 oxidation. Thus, from an industrial point of view, the NH_3 oxidation in its mixtures with H_2 at high pressure has certain emissions advantages compared to its mixtures with hydrocarbons (e.g. CH_4) as less N_2O production for the same experimental conditions and, as mentioned before, less NO additionally to zero CO_2 emission. Fig. S11 - S13 of the supplementary material show the N_2O, NO, and NO_2 conversion for the studied conditions.

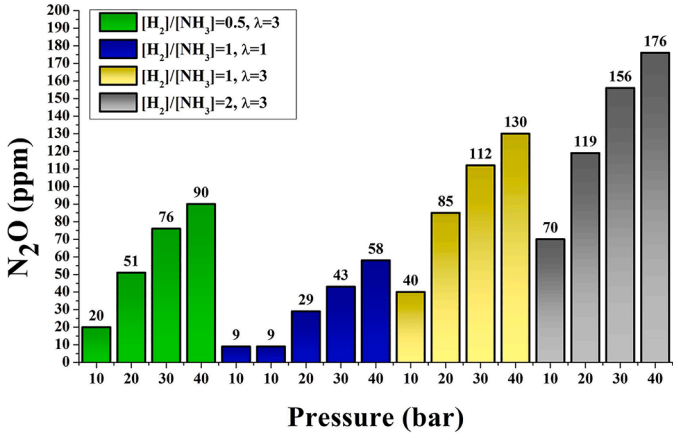

Fig. 3. N_2O production as a function of temperature in all studied conditions, sets 1–16 in Table 1.

3.4. Sensitivity analysis

Sensitivity analyses have been performed to identify the most important reactions that control the oxidation of NH_3/H_2 mixture, Fig. S6-S9 in supplementary material. NH_3 and H_2 consumption are promoted by reactions that produce H through reactions of H_2 with OH and NH_2, $NH_2 + H_2 \rightleftarrows NH_3 + H$ (-R4) and $OH + H_2 \rightleftharpoons H + H_2O$ (6), and by reaction $NH_3 + HO_2 \rightleftharpoons NH_2 + H_2O_2$ (R21) that produce NH_2. NH_3 and H_2 consumption are also promoted by reactions that produce OH via NH_2 reaction with NO (R14) and HO_2 (R22), through the decomposition of H_2O_2 (+M) (R23) which is more relevant under oxidizing conditions and 40 bar, and through the reaction $H + O_2$ (R12) which also produces O radicals and is more important at 10 bar. Finally, some important promoting reactions that lead to the HO_2 production include: $H_2O_2 + H$ (R24), $HNO + O_2$ (R25), $H + O_2$ (+M) (R8), $H_2NO + O_2$ (R26), and to HNO production: the latter one (R26) and $H_2NO + NO_2$ (R27). It is noted that NH_3 and H_2 consumption is promoted by reactions that produce NH_2, H, OH, O, HO_2 and HNO. Under the same experimental conditions, the H_2O production reactions via $NH_3 + OH$ (R3) and via NO_x (NO and NO_2) reactions with NH_2 to form $N_2 + H_2O$ (R13) and $N_2O + H_2O$ (R19), which are favored by pressure, inhibit the consumption of NH_3 and H_2. NH_2 reactions with H_2NO (R28) and HO_2 (R29) to form NH_3, which are important under oxidizing conditions, also appear as inhibitory reactions. The recombination of HO_2 (R30) to form $H_2O_2 + O_2$ which competes with promoting reactions (R21) and (R22) also has a negative impact. We also detected that NO_2 reactions with H, HNO and NH_2 to form NO + OH (R17), $H_2NO + NO$ (R18) and NO + HONO (R31) have an inhibitory behavior, as well as the NH_2 oxidation to produce H_2NO (R32). It is important to remark that reaction $H + O_2$ (+M) (R8) to form HO_2, also appears as inhibitory but only for $H_2/NH_3 = 1$ and 10 bar conditions. It can be concluded that NH_3 and H_2 conversion is inhibited by reactions that involve H_2O, NH_3, NO, H_2NO and O_2 production. According to model calculations, the presence of H_2 in the NH_3/H_2 mixtures makes the influence of O/H radicals to become more significant compared to the conversion of net NH_3, even when small amounts of H_2 are added, as reported in the literature [16,17].

3.5. N balance

Fig. 4 shows the N atoms balance of the different experiments to evaluate its quality and to determine if the measured species are dominant under the studied conditions. The N balance is calculated considering the following species: NH_3, N_2, NO, N_2O, and NO_2. Although NO and NO_2 have been accounted for in the N balance, these species are around the uncertainty of the equipment below 5 ppm in most cases.

The N balance (in percentage) of the species mentioned calculated with the model is also shown in Fig. 4 as a continuous line that closes at 100% while the experimental N balance closes between 95 and 105% along the whole temperature range. This indicates a great agreement with determined and calculated species and also that the species measured are the predominant ones. Fig. S14 of the SM shows the N balances for the rest of the studied conditions.

4. Conclusions

An experimental and simulation study of the oxidation of mixtures of NH_3 and H_2 at high pressure (from 10 to 40 bar), under stoichiometric and oxidizing conditions in the 250–1250 K temperature range, in a quartz tubular flow reactor with 1000 ppm of NH_3 and 500, 1000 and 2000 ppm of H_2, using argon as a diluent, has been performed.

The main product of NH_3/H_2 mixture conversion is N_2, followed by N_2O, while NO and NO_2 concentrations are negligible and below the detection limit under all the conditions studied. The use of high pressure acts to favor the formation of N_2 from NH_3 oxidation compared to what happens at atmospheric pressure. This is a positive outcome for the use of NH_3 as a fuel in high pressure applications, such as turbines.

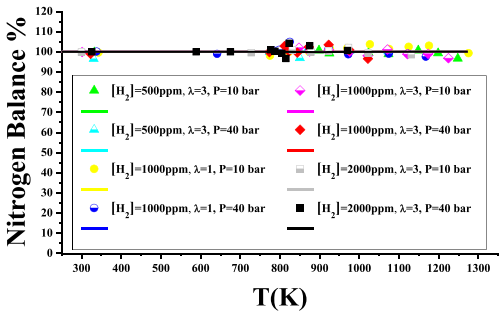

Fig. 4. N balance as a function of temperature, sets 1, 4, 5, 8, 9, 12, 13 and 16 in Table 1.

Nevertheless, the N_2O production in the exhaust gases is significantly higher than in pure NH_3 oxidation and lower than in NH_3/CH_4 mixtures.

The onset of both NH_3 and H_2 oxidation occurs at lower temperatures for oxidizing conditions compared to stoichiometric ones, for all the studied pressures, indicating the importance of stoichiometry.

The presence of H_2 also acts to shift NH_3 conversion to lower temperatures, up to 250–350 K, compared to pure NH_3 oxidation.

Pressure has a clear influence on both NH_3 and H_2 oxidation regimes, shifting them to a lower temperature as pressure increases. As can be seen, the influence of pressure is more remarkable at low pressures, compared to high ones, and simultaneously this influence is lower at higher H_2/NH_3 ratios.

Reactions that produce NH_2, H, OH, O, HO_2 and HNO species favor the NH_3 and H_2 consumption. On the other side, inhibition of NH_3 and H_2 combustion is powered by reactions that produce H_2O, NH_3, NO, H_2NO and O_2, under the studied conditions.

The literature mechanism, used for simulations, is able to describe quite well the H_2 and NH_3 conversion trends under most of the studied conditions.

Novelty and significance statement

The novelty of this research is the experimental and simulated study of ammonia-hydrogen mixtures at high pressure in a plug flow reactor. To our knowledge, there are no previous studies in the literature like the present ones at high pressure (from 10 to 40 bar). It is significant, first of all, because this range of pressures is representative of turbines and engines in the industry and directly helps to understand and improve the implementation of technologies based on carbon-free combustion. Also, the extended database of experimental results of the present work is helpful for model improvement and validation.

Author contributions

P.G.: Designed research, Performed experiments and calculations, Analyzed data, Wrote the manuscript. **M.A.:** Performed experiment. **D. C.:** Performed experiment. **R.B.:** Designed research, Analyzed data, Research Supervision. **M.U.A.:** Designed research, Analyzed data, Research Supervision, Wrote the manuscript.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.proci.2024.105726.

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