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Combustion Regimes and Chemical Kinetics of Ammonia

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Results presented in the current thesis have been published in scientific journals of international relevance:

- 1. Manna, M. V., Sabia, P., Ragucci, R., & de Joannon, M. (2020). Oxidation and pyrolysis of ammonia mixtures in model reactors. *Fuel*, *264*, 116768.
- 2. Sabia, P., Manna, M. V., Cavaliere, A., Ragucci, R., & de Joannon, M. (2020). Ammonia oxidation features in a Jet Stirred Flow Reactor. The role of NH2 chemistry. *Fuel*, 276, 118054.
- 3. Sabia, P., Manna, M. V., Ragucci, R., & de Joannon, M. (2020). Mutual inhibition effect of hydrogen and ammonia in oxidation processes and the role of ammonia as "strong" collider in third-molecular reactions. *International Journal of Hydrogen Energy*, *45*(56), 32113-32127.
- 4. Manna, M. V., Sabia, P., Ragucci, R., & de Joannon, M. (2021). Ammonia oxidation regimes and transitional behaviors in a Jet Stirred Flow Reactor. *Combustion and Flame*, 228, 388-400.
- 5. Manna, M. V., Sabia, P., Ragucci, R., & De Joannon, M. (2021). Thermokinetic Instabilities for Ammonia-hydrogen Mixtures in a Jet Stirred Flow Reactor. *Chemical Engineering Transactions*, *86*, 697-702.
- Manna, M. V., Sabia, P., Sorrentino, G., Viola, T., Ragucci, R., & De Joannon, M. (2022). New insight into NH₃-H₂ mutual inhibiting effects and dynamic regimes at low-intermediate temperatures. *Combustion and Flame*. <u>https://doi.org/10.1016/j.combustflame.2021.111957</u>
- Manna, M. V., Sabia, P., Shrestha, K. P., Seidel, L., Ragucci, R., Mauß, F., & De Joannon, M. (2022). NH₃-NO interaction under low-temperatures: an experimental and modeling study. Submitted to *Proceedings of the Combustion Institute*.

The thesis develops through a compact and sequential re-elaboration of the work reported in the above-mentioned publications.

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ABSTRACT

The compelling requirement to reduce greenhouse gas emissions has led the scientific community to explore alternative energy sources, in particular energy vectors with a minor impact on the environment. The long-term chemical storage represents a key element for the decarbonization of the energy system, to guarantee security and flexibility to the power generation based on renewable sources. In this context, in recent years the interest of the scientific community has been focused on energy vectors whose production and use are able to meet the zero emissions target.

Among the available molecules, ammonia is a high density hydrogen carrier and has the advantage of being a carbon-free carrier, with existing delivery infrastructures, consolidated production technologies and well-defined regulations. Ammonia can be efficiently cracked by catalytic processes to recover the hydrogen with high purity. Recently, the interest in ammonia as fuel itself has grown up as well. Nonetheless, while the advantages of ammonia are indisputable, it is known that its combustion properties, as well as the high NO_x emissions, represent a serious drawback for its use in conventional combustion processes. Different strategies have been suggested to overcome these limits. Blending ammonia with carbon-based fuels has been proposed as plausible solution to improve ammonia performances in ICEs, boilers and gas turbines. These strategies allow to increase combustion efficiencies and mitigate NO_x emissions, but compromise the development of a totally carbon-free energetic system, thus forcing to deal with CO and CO₂ emissions. Alternatively, the use of hydrogen as a fuel enhancer can bypass this last drawback. However, this solution comes at a higher NO_x specific emission.

Due to the above-reported issues, the utilization of pure ammonia as a fuel can only be practicable by implementing new combustion modes. MILD combustion has been proven to be a suitable process to burn ammonia without the addition of fuel enhancers, with low-NO_x emissions. The successful application of ammonia as alternative fuel under diluted and pre-heated conditions requires a detailed understanding of its oxidation process. To this aim, several efforts have been recently dedicated to the oxidation characteristics in simple reactor configurations for the evaluation of laminar flame speed, ignition delay times and ammonia oxidation regimes, along with key species and NO_x productions in a wide range of operative conditions.

The definition of basic characteristics of the ammonia oxidation chemistry has boosted also the development of detailed kinetic mechanisms. Despite all these efforts, the comprehension of the ammonia oxidation chemistry cannot be considered mature. This aspect is even more evident if referring to MILD operative conditions, where high dilution levels impose fuel oxidation to occur under low temperature regimes. The intersection of low combustion temperatures with diluted mixtures alters the evolution of the combustion process with respect to traditional flames, affecting the kinetics involved in fuel oxidation. Due to this background, the present thesis deals with an experimental and numerical characterization of ammonia oxidation in a Jet Stirred Flow Reactor. The experimental analyses have been carried out at nearly atmospheric pressure, covering a wide range of operative conditions. The combustion behavior of ammonia mixtures diluted in Ar and N_2 was investigated for temperatures in the range 900-1350K, changing the mixture equivalence ratio from fuel-lean to fuel-rich conditions. Different dilution levels were considered in order to promote the mixture ignition in diverse temperature ranges, bringing to the light peculiar combustion behaviors. Indeed, high dilution levels (<99%) shift the ignition at high temperatures, due to the lower thermal power of the reactant mixtures. On the other hand, a moderate level of dilution, and thus higher fuel concentrations, promote the oxidation process at lower temperatures, favoring completely different kinetic paths. Such operating conditions are also particularly relevant for applications in engines and gas turbines.

Temperature and species concentration measurements at steady state condition revealed for the first time the existence of different combustion regimes, namely low, intermediate and high temperature oxidation regimes. At low-intermediate temperatures, H₂ and NO concentrations exhibited a non-monotonic trend as a function of the inlet temperatures, independently of the mixture composition, while for higher temperatures the system behavior was more strongly affected by the mixture stoichiometry.

The oxidation process was then investigated through transient experimental tests, following the evolution of the reactor temperature in time. These analyses allowed to identify further peculiar behaviors like low-reactivity regime, damped and periodic oscillations, occurring at noticeable temperatures. Such phenomena were deeply explored changing the mixture composition, the residence time, the dilution level and diluent species.

The effect of doping ammonia mixtures with NO was also explored in order to highlight the role of NO formation and reduction in ammonia oxidation chemistry.

The interaction between ammonia and hydrogen oxidation chemistry was then investigated, highlighting the enhancing role of hydrogen at high temperatures and a peculiar mutual inhibiting interaction of such fuels under low-temperature conditions. The inhibiting effect of ammonia on hydrogen oxidation suggested, for the first time, the plausible role of such molecule as strong collider in third-body reactions, given its physical/chemical properties. This aspect could cover a key-role to improve kinetic models performances for the investigated conditions.

Numerical simulations were carried out by means of several kinetic models available in literature. It was shown that kinetic models are able to reproduce the experimental data at high temperature (higher than 1300K), whereas they fail to describe the low temperature reactivity, with severe implications also on the prediction of dynamic behaviors.

Kinetic analyses were performed to identify the controlling reaction pathways. It was found that the low-temperature oxidation chemistry depends on different NH₂ consumption routes promoted in diverse temperature ranges, whose description changes mechanism by mechanism. In particular, models that envisage the oxidation of ammonia through recombination routes predict higher reactivity at low temperature and the insurgence of instabilities, that derive from a strong competition between NH₂ oxidation and recombination routes.

Based on the obtained experimental data and numerical analyses, a final effort to model ammonia oxidation was made, improving the performance of an existing detailed kinetic mechanism through the implementation of new reactions and the tuning of the kinetic parameters of the most sensitive ones. The declaration of third-body efficiency for ammonia was essential to correctly reproduce the non-monotonic profiles of the main species in the low-intermediate temperature regime.



1. INTRODUCTION

1.1. Chemical energy storage for carbon neutral energy system

The world energy demand is currently facing with the constraint to reduce the Green Houses Gases (GHG) emissions due to the global warming acceleration. The Paris Agreement adopted at the Conference of Parties 21 (COP21) establishes the goal to reduce the increase in the global average temperature to below 2°C and each signatory Nation proposes its Intended Nationally Determined Contribution (INDC) [1]. Specifically, the Climate Action launched by European Union has the target to reduce the GHG emissions by 80-95% until 2050.

The World Energy Outlook 2020 [2] identifies the global energy trends and their potential impact on supply and demand, carbon emissions, air pollution and energy access. From the analysis modelled in the New Policies Scenario emerges that the energy demand is expected to grow by more than 25% to 2040, under current and planned policies. Indeed, a huge transformation is assaulting the electricity market because of the increasing demand brought by the digital economy, electrification in transportation and other technologies.

In this context, whatever energy supply system have to face with the compulsory criteria defined by the World Energy Council, which delineates the so-called *Energy Trilemma* [3]:

- Energy Security, in terms of effectiveness of energy supply;
- Energy Equity, in terms of energy availability across the population;
- Environmental Sustainability, in terms of low carbon and efficiency.

Several efforts are needed to increase the low-carbon sources of power, ensuring the energy sustainability.

Nowadays, due to supportive government policies, the Renewable Energy Sources (RES) are significantly emerging, to the extent that they could provide almost two third of the global capacity additions to 2040 [2]. The promotion of the RES relies on related technologies that, unfortunately, are strictly dependent on the so-called critical metals. A metal is perceived as critical if it is crucial for green energy technologies and if it is scarce in terms of reserves and resources [4,5].

Specifically, serious problems can arise in the solar energy sector, since photovoltaics and Concentrated Solar Power technologies are seriously affected by the availability of silver, indium, tellurium and ruthenium. Such materials display unique characteristics for specific applications and usually cannot be substituted one for another. Similar consideration applies for the wind energy supply chain and electromobility sector [4].

In several cases, the available global mineral reserve is insufficient to cover the demand of metals [5], which are needed for meeting the 2050 energy scenario of the Intergovernmental Panel on Climate Change. The gap could be filled by means of metal

recycling, thus facing with the available technologies for recycling and with the rate of end of life recycle.

It is worth to highlight that these aspects could threaten geopolitical equilibria and have a strong socio-environmental impact for the mining of mineral to extract the metals.

Moreover, significant limitations come from the intermittence of the VRES and on their dependence on geography and weather conditions, thus posing the question of power distribution from the production to the consumption point, by means of efficient storage (with as little loss as possible) and transportation over long distances [6]. Currently, mechanical, chemical, thermal and electrical technologies are available for storing electrical energy from small to large scale applications. Among them, Compressed Air Energy Storage (CAES) and Pump Hydro are limited by geographic/geological requirements, whereas the electrical technologies have not enough commercial maturity and the ability for large scale applications over long periods of time. Therefore, the transformation of the energy industry towards a climate-neutral circular economy [6] is only feasible including the chemical energy carriers and the processes for the thermochemical and electrochemical energy conversion. Indeed, the long-term energy storage in a chemical form represents a key element for the decarbonization of the energy system, to guarantee security and flexibility to the power generation based on renewable sources [7]. The energy stored in a chemical form is more economical and benefits of higher storage capacity and longer discharge time duration if compared with electrochemical, mechanical or thermal energy storage, as schematically reported in Figure 1 [6].



Figure 1. Overview of storage capacity and discharge duration of storage technologies (from Dreizler et al. [6]).

Therefore, the energy surplus from the RES can be converted into new and smarter fuels, including in this category any solid, liquid or gaseous material that can be oxidized. Such synthetic fuels can be carbonaceous (natural gas and biofuels) or carbon-free (hydrogen,

ammonia, metals, some metalloids and non-metals). How to utilize economically, efficiently, and eco-friendly these energy carriers is currently subject matter of research. Despite the several recent efforts for the establishment of fuel cells and redox flow batteries on the energy market, such processes are growing slowly with respect to the well consolidated thermochemical energy conversion [6]. Indeed, the integration of combustion processes in the energy mix can support the deployment of RES because it is the only reliable process with the appropriate characteristics (i.e. response and duration time, power supply, fuel flexibility) and existing infrastructures able to fill the gap of the RES intermittency, in short and long term perspectives.

1.2. The role of MILD combustion as a thermochemical energy conversion processes

The introduction of new alternative fuels poses new challenges, despite the traditional combustion processes benefit of a deep knowledge and consolidated technologies. Combustion characteristics like flame speeds, ignition delay times, flammability limits, ignition temperatures, and adiabatic flame temperatures can be considerably different for this kind of molecules if compared with conventional fuels, with implications on process efficiency, safety and pollutant emissions. Complications such as flame flashback, blowout, incomplete fuel conversion must be handled properly. Therefore, innovative combustion technologies are needed in order to face the requirements imposed by the new and complex energy scenarios, satisfying the criteria of sustainability and fuel-flexibility, assuring high efficiency, stable combustion and low pollutant emissions for a wide range of operative conditions.

Among the processes and technologies that may help overcoming the abovementioned obstacles, MILD (Moderate or Intensive Low-oxygen Dilution) combustion has been recognized as plausible candidates for stationary applications, like furnaces and boilers, and it could be potentially used into many other applications, such as gas turbines or for combined heat and power (CHP) units and engines (critical issues of chemical kinetics). According to the definition given by Cavaliere and de Joannon [8], a combustion process is named MILD when the inlet temperature of the reactant mixture is higher than mixture self-ignition temperature and the maximum allowable temperature increase with respect to inlet temperature during combustion is lower than self-ignition temperature (in Kelvin). Unlike the traditional oxidation processes, that are characterized by a high heat release sufficient to sustain the minimum temperature required for a stable oxidation, MILD combustion evolves through distributed spontaneous ignition based on local ignidiffusive structures [8], by reason of the local/inlet high diluted and preheated conditions. Indeed, to achieve such operative conditions, MILD combustion envisages the use of mixtures highly diluted and pre-heated by an internal or external recirculation of mass and sensible enthalpy within the combustion system.

In these way, system working temperatures are levelled to values not critical for undesired species production (e.g. NO_x , particulate matter) by regulating the hot exhausted gas recirculation within the combustion chamber, as they dilute fresh reactants. Therefore, combustion adiabatic temperatures are lowered without compromising process stability. This is mainly due to sensible enthalpy feedback to pre-heat reactants, by means of exhausted gas recirculation strategies, in order to increase the temperature of fresh reactants/recirculated exhaust mixture above the autoignition values [9].

Such a strategy guarantees high resiliency to the extinction and high flexibility with respect to the fuel chemical/physical properties. Indeed, until now, the successful use of MILD combustion has been proven for a wide palette of energy carriers, from synthetic gas and/or bio-derived fuels to no-carbon species (hydrogen, ammonia) [10–14].

The shift from traditional deflagrative/diffusive flames to an oxidation process controlled by mixtures autoignition under moderate temperature has strong implication on the chemical aspects of the oxidation process. The relatively low working temperature coupled with the high dilution level reduce the characteristic chemical times, thus promoting the establishment of peculiar reacting structures within combustion chambers, as extensively reported in the reviews [12,15].

Furthermore, the great amount of species such as water and carbon dioxide impacts the kinetic routes, through thermal and kinetic effects [12]:

- Thermal effect: higher thermal capacity of such molecules with respect to N₂;
- Kinetic effect: these molecules participate directly in bi-molecular reactions and as strong collider in ter-molecular reactions, due to the higher collisional efficiency with respect to N₂.

All these aspects have to be taken into account in the development of detailed oxidation mechanisms for MILD combustion processes.

1.3. Ammonia as carbon free energy vector

In recent years the interest of the scientific community has been focused on energy vectors whose production and use are able to meet the zero emissions target. The Committee on Climate Change [16] recognizes hydrogen as a plausible candidate, since it could be produced from natural gas with Carbon Capture and Sequestration technologies (blue hydrogen) [17,18] or directly from water electrolysis (green hydrogen) [18–20].

The role of green and blue hydrogen (from renewable sources) as an energy carrier for stationary and transport applications is recognized as the main leading challenge [21–23]. Hydrogen is very often supposed to be the ideal fuel because of its high heat value (on mass basis) and the absence of CO_2 emissions.

Nonetheless, the attempt to reach an energy system based on the hydrogen economy is a long-term project, that mandatorily will require several sequential adaptations, encompassing the exploitation of different intermediate energy vectors and the development of the most appropriate enabling technologies to ensure a safe and sustainable hydrogen use. The long-term nature of this scenario depends mainly on the difficulties to properly burn hydrogen, limiting NO_x emissions, and to store and safely transport it, due to H₂ physical/chemical properties. In hydrogen-air oxidation processes, the high adiabatic temperature has to be controlled to limit the formation of thermal-NO_x. This requires the implementation of new non-traditional combustion systems. On the other hand, hydrogen low energy density (on a volume basis) implies the necessity to pressurize or liquify it for an effective storage/transport. This requirement, along with safety issues related to hydrogen highly flammability range, strong propensity to explosion and high diffusivities into the atmosphere, make it very difficult to transport and store, without bearable economic solutions [22,23].

Given this background, the H₂ conversion to other energy vectors more easily transportable and with high-energy density [22,23] represents a relatively cheap alternative capable of guaranteeing energy supply within the constraints of the energy trilemma [24–27]. Indeed, there are several mature technologies capable of converting hydrogen to other energy vectors [24,28] as, for instance, carbonaceous, as synthetic methane or syngas using carbon dioxides from biogas\power\chemical\bio-logical plants [28,29], methanol [30], high molecular weight hydrocarbons [31], carbon free ammonia and related chemicals (hydrazine, urea, ammonia carbonate) [32–34].

The International Energy Agency (IEA) has recently become a great promoter of ammonia as enabler of hydrogen economy and several countries have started rising the awareness of ammonia potentials, thus boosting the research for its use as hydrogen vector and potential fuels. The Japan Science and Technology (JST) Agency has declared the intention of becoming leadership of the country in ammonia production and use, recognizing the leading role of the chemical storage in the transition towards renewable alternatives. In the USA, the ARPA-E announced that substantial funding will be allocated to 13 projects focused on ammonia. In the UK, the synergistic work between universities and companies is going to design and commission a first "Green Ammonia Decoupled" device, for the conversion of wind into ammonia and the successive energy release *via* internal combustion engines. Yara, the second biggest ammonia produces, intends to produce ammonia from solar energy in Western Australia.

There are several benefits that make ammonia worth of a careful evaluation on its potentials as hydrogen carrier and energy vector. Ammonia has several advantages over hydrogen, like lower cost per unit of stored energy, higher volumetric energy density and it can be easily liquefied at 0.8MPa at ambient temperature. Furthermore, it benefits of widespread and consolidated production technologies and commercial viability [32–38]. For more than 100 years, since the Haber-Bosh process was introduced, ammonia has been used as fertilizer in the agricultural sector, as raw material for various industrial products, as refrigerant in industrial coolers, as additive in NO_x abetment processes (Selective Catalytic Reduction, SCR, and Selective Non-Catalytic Reduction, SNCR [39]). Due to its several applications, consolidated infrastructures for ammonia transport and storage are available.

Over 200 million metric tons of ammonia per annum are produced worldwide [40]. At present, ammonia is still produced through the well-established Haber-Bosh process, which is known to be very energy and capital intensive and not environmental sustainable, since the Haber-Bosch process is strongly reliant on fossil fuels. Indeed, ammonia is derived from nitrogen and hydrogen, reacting together in catalytic reactors, under high pressure (10-25MPa) and temperature between 623-823 K. The high purity hydrogen is mainly produced from the steam reforming of natural gas and partial oxidation of coal, thus the process is highly carbon intensive accounting for 290Mt/year of CO₂. Despite the integration of Carbon Capture and Sequestration (CCS) processes, the production of "brown ammonia" is definitely detrimental for the environment, therefore new technologies are desirable for obtaining hydrogen from alternative sustainable sources, such as the electrolysis of water using energy from solar, biomass, wind. The electrochemical routes could potentially reduce the energy input by more than 20% and could reduce the complexity and cost of the conventional ammonia production process [41]. Furthermore, the electrochemical synthesis of ammonia directly from H_2O and N_2 could bypass the hydrogen production chain [42,43].

Nonetheless, the current production of ammonia from the electrolyzed water represent only the 0.5% of the global ammonia production, due to the high costs related to this process. Further research need to be undertaken for more economical solutions to produce "green ammonia", in order to make the entire production-utilization ammonia cycle completely carbon-free.

The interest in ammonia has been recently growing on its potential role as fuel, to support power and heating processes. The first early attempts to use ammonia for power generation dates back to the industrial revolution, when inventors proposed ambitious designs for ammonia-fuelled electrification and gas locomotives. However, it was not until the 20th century that ammonia was first used as a fuel. During the World Wars I and II, in Germany and Belgium, shortages of diesel and oil led to the development of ammonia-fuelled engines [44]. Although this attempt was abandoned at the end of the war, these pioneering experiments served to demonstrate that ammonia could be considered for energy production.

Nowadays, the use of ammonia for power generation is still under research. Indeed, while all these abovementioned benefits make ammonia a promising candidate as hydrogen carrier, its corrosive nature and scarce combustion properties represent a hindrance to its practical use in both stationary plants and transportation systems [45–53].

For instance, Table 1 compares ammonia combustion properties with methane, methanol and hydrogen [44]. It is evident that its low laminar burning velocity and heating value combined with high auto-ignition temperature and minimum ignition energy make the oxidation of pure ammonia difficult in practical applications.

	Methane	Hydrogen	Methanol	Ammonia
Density (kg/m ³)	0.66	0.08	786	0.73
Dynamic viscosity $\times 10^{-5}$ (P)	11	8.8	594	9.9
Low heating value (MJ/kg)	50.05	120	19.92	18.8
Laminar burning velocity (m/s) – close to stoich.	0.38	3.51	0.36	0.07
Minimum ignition energy (mJ)	0.28	0.011	0.14	8
Auto-ignition temperature (K)	859	773-850	712	930
Octane number	120	-	119	130
Adiabatic flame temperature (with air) (K)	2223	2483	1910	1850
Heat capacity ratio, $\overline{\gamma}$	1.32	1.41	1.2	1.32
Gravimetric Hydrogen density (wt %)	25	100	12.5	17.8

Table 1. Ammonia combustion characteristic and comparison with other fuels, at 300K and 0.1MPa. Adapted from [44].

The low reactivity of ammonia is problematic for gas turbine, as it requires to increase the average residence time, by decreasing the flow rate. This, in turn, affects the level of turbulence of the combustion chamber with direct consequences on the combustion efficiency [54].

Despite its high octane number makes ammonia attractive for fuelling internal combustion engines (ICE), the low laminar flame speed is not advantageous for spark-ignition engines, since it can induce large amount of unburned gas and, potentially, knocking. Moreover, the high resistance to ignition in compression-ignition engines would require extremely high compression ratios.

Blending ammonia with other fuels represents a feasible solution to use NH₃ for power generation.

Studies on ammonia/diesel mixtures in engines showed that peak torque could be achieved, reducing CO_2 emissions by systematically increasing NH_3 concentration up to 60-70%. Higher NH_3 content would boost the NO_x production to undesirable values.

The Korean Institute for Energy Research is a great promoter of the ammonia dual-fuel strategy. Indeed, it has proposed the AmVeh, a new concept for ammonia fuelled engine, with the aim to convert the existing vehicles into 70% NH₃-30% gasoline vehicles, through the installation of control system and the removal of corrodible metals [55].

Other carbon based fuel/ammonia blends like gasoline/ammonia, ethanol/ammonia, ammonium nitrate/ammonia and dimethyl ether/ammonia have been investigated, with promising results in terms of power output, although with high NOx emissions [44].

Evidently, the oxidation of NH_3 - H_2 mixtures is more attractive within the perspective of a carbon-free energy production system, also considering that hydrogen can be direct produced from ammonia partial cracking [56,57].

Under high temperature conditions, hydrogen has an accelerant and stabilizing role in H₂-NH₃ combustion. In particular, due to its high diffusivity and heating value, hydrogen addition improves NH₃ burning velocity [58–60] and ensures combustion stability for wider equivalence ratios [61,62].

Indeed, ammonia partial dissociation allows to attain similar properties to some common hydrocarbons, thus make such mixtures suitable for energy production in gas turbine systems, however at the expanse of higher NO_x emissions, particularly under fuel lean conditions, thus requiring the integration of Selective Catalytic Reduction (SCR) for the exhaust gases.

The utilization of pure ammonia as a fuel can only be practicable by implementing new combustion modes. MILD combustion [63] has been proven to be suitable to burn ammonia without the addition of fuel enhancers [64–66]. Sorrentino et al. [13] demonstrated that the oxidation of ammonia in a cyclonic MILD burner is stable for working temperature above 1350K and low-NO_x emissions (lower than 10 ppm) have been measured under the investigated operating conditions. Extinction phenomena take place at temperatures lower than 1300K and the transition from burning to unburning conditions occurs through instabilities. Indeed, low-intermediate temperature oxidation chemistry, coupled with heat exchange phenomena, could promote the onset of thermokinetic instabilities. They could have detrimental effects on process energy efficiency and pollutant emissions. For instance, these phenomena in gas turbine applications may also boost the onset of thermo-acoustic instabilities and possible mechanical damages [67–71]. For these reasons, the establishment of such behaviors must be extensively studied, through a deep comprehension of ammonia oxidation chemistry.

2. COMBUSTION CHEMISTRY OF AMMONIA

2.1. State of the art

The development of combustion-based technologies for ammonia utilization requires a deep comprehension of its detailed combustion chemistry under several operative conditions. Therefore, in the last decade, several research has been dedicated to understand the fundamental characteristics of ammonia oxidation and the complex reaction pathways that occur throughout its combustion process.

In 1960s, the early studies were performed to understand the chemical reactions of flames containing ammonia, due to its importance in NO_x formation and reduction. The first complete description of ammonia oxidation was proposed by Miller and Bowman [72], with special emphasis on the performance of the NO_x chemistry. Therefore, in the next Paragraph 2.1.1 the well-known mechanism for NO_x removal through NH_3 is discussed, before analyzing the recent findings on ammonia combustion chemistry (Paragraph 2.1.2).

2.1.1. NH₃ as DeNOx agent for the Selective Non-Catalytic Reduction

The role of ammonia as reducing agent for nitrogen oxides in combustion processes has been deeply investigated [73–76]. Due to the high selectivity of the NH₂ radical with respect to NO_x, even in presence of O₂ in the gas-phase, NH₃ and urea are the perfect candidates for NO_x abetment through Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR).

SNCR using NH_3 as the reducing agent was developed by Lyon [73,74] who named the process Thermal $DeNO_x$

The SNCR is a conceptually simple process for NO_x control. For temperatures between 1100K and 1400K, a reducing reagent (NH₃ or urea) is injected and mixed in a flue gas stream containing NO_x and a rapid gas phase homogeneous reaction occurs. In spite of the presence of excess oxygen generally required, the reagent selectively reduces NO, leaving oxygen largely unreacted. The technology is attractive due to its simplicity: catalyst-free system (and hence free of associated problems), ease of installation on existing plants, lower capital and operating cost.

Due to the involvement of NH_3 as reducing agent and to the presence of O, H, OH radicals in the gas phase, the understanding of the controlling chemistry of such a process has been a benchmark for the development of a detailed kinetic mechanism for ammonia oxidation.

Characteristic of the process is that nitric oxide removal is possible only in a narrow temperature range centered at 1250 K, termed as the "DeNOx temperature window" [39]. Indeed, at temperatures below 1100 K, the reaction is too slow to give any reduction and most of the injected NH₃ remains unreacted, while above 1400K NH₃ tends to oxidize to

form NO rather than to reduce it, as reported in Figure 2 from [39].



Figure 2. Temperature window of SNCR process using NH_3 at molar ratio $NH_3/NOx=1.5$. Adapted from [39].

The controlling chemistry of the DeNOx is herein discussed, according to the detailed description of the process provided in [39,62].

The NO reduction starts through the formation of NH_2 radical through the reactions of NH_3 with the O/H radical pool, primarily OH, according to the following reactions:

(R1) NH3+OH=NH2+H2O

(R2) NH3+O=NH2+OH

The formation of NH_2 radical is the key step in the process since, despite the oxidizing environment, the high selectivity of NH_2 with respect to NO allows the NO reduction within the DeNO_x temperature window through the reactions:

(R3) NH₂+NO=N₂+H₂O

(R4) NH₂+NO=NNH+OH

In particular, the reaction R3 is chain terminating, while R4 simultaneously reduces NO and produce OH radical. Furthermore, the dissociation of NNH initiates a reaction sequence, which secures the net formation of three hydroxyl radicals:

(R5) NNH=N₂+H

(R6) H+O₂=OH+O

 $(R7) O+H_2O=OH+OH$

where reactions R6 and R7 control the chain branching mechanism.

Since the reaction NH₂+NO has two product channel, it is possible to define the branching ratio as follow:

 $\alpha = k_{R4}/(k_{R3}+k_{R4})$

For the self-sustainability of the overall process, it is required that α must be at least 25%. In the temperature range 1100-1400K, α attains values of 0.3-0.4.

At higher temperatures, the chain branching mechanism becomes significantly faster, thus leading to a strong growth in the O/H radical pool. As a consequence, the OH radicals interact with NH₂ through the reaction:

(R9) NH2+OH=NH+H2O

which becomes competitive with the R3 and R4. The NH formed is partly oxidized to NO through the sequence $NH \rightarrow HNO \rightarrow NO$, in particular, NH radical is converted to NO, according to the reactions:

(R10) NH+O2=HNO+O

(R11) NH+O₂=NO+OH

(R12) NH+OH=HNO+H

(R13) HNO+OH=NO+H₂O

Also the NH₂+O reaction contributes to increase the NO concentration, through a net formation (for temperature typically around 1400K) or the production of HNO.

On the contrary, for lower temperatures reactions R6 and R7 are too slow, thus OH concentration decreases and NH₃ is not promptly dehydrogenated to NH₂.

For this reason, the termination reactions R3, R15, R16 occur, where:

(R15) NH₂+HNO=NO+NH₃

(R16) HNO+OH=NO+H2O

thus leading to a reduced efficiency in NO reduction.

 NO_2 and N_2O formation has to be carefully considered in the Thermal DeNOx process. The formation of NO_2 is strongly affected by the concentration of O_2 in the gas-phase, as it is formed in significant quantities at high O_2 concentrations and decreases rapidly as O_2 level decreases.

Nitrogen dioxide is formed through the sequence:

NNH+O₂=N₂+HO₂

NO+HO2=NO2+OH

And it is subsequently re-converted to NO according to the reaction:

NH2+NO2=H2NO+NO

The formation of N_2O depends on both temperature and O_2 concentration. Indeed, the N_2O peak shifts from high to low temperature as O_2 concentration increases. The reactions responsible of N_2O formation are:

 $NH_2+NO_2=N_2O+H_2O$

 $NH+NO=N_2O+H$

The first reaction is active at low temperatures and high O_2 concentration. The latter competes with NH+O₂ at higher temperature and lower O₂ concentration.

Despite literature is plenty of works concerning the thermal DeNO_x mechanism and the main features of the process are satisfactorily described by the available kinetic models, the level of accuracy for the reactions NH₂+NO (around 10%) is still not sufficient to guarantee a good prediction of NO emissions. Indeed, even a small correction of the branching ratio α has a great impact on the models prediction [62].

2.1.2. NH₃ oxidation chemistry

In the 1980s, Miller and Bowman [72] proposed the first detailed kinetic mechanism for ammonia combustion. The model was validated against several experiments and the comparison between the theoretical kinetic model and experimental data showed good

performance over a wide range of temperatures, equivalence ratios and pressures, in particular for the prediction of NO_x .

Based on Miller's work, other mechanisms have been developed across the years.

Lindstedt et al. [77] developed a kinetic mechanism for the prediction of flat laminar flames for ammonia oxidation, with special emphasis on the reaction pathways for NO_x formation for both pure ammonia and ammonia hydrogen mixtures. In particular, they assessed the key role of the reaction paths NH+OH in NO formation when using pure ammonia.

Skreiberg et al. [78] developed a kinetic model for ammonia in presence of methane, hydrogen and carbon monoxide, based on the H/N/O sub-mechanism of Miller's work. Several reactions were characterized accurately, giving a model capable of satisfactorily predicting flow reactor measurements data.

Konnov's kinetics model [79] was originally developed for the combustion of small hydrocarbon fuels doped with ammonia. In the latest version, the H/N/O sub-mechanism and the NCN pathway were updated. It has been tested against experimental data for oxidation, ignition and flame structures in mixtures containing nitrogen species, showing a good performance on the prediction of NO_x emission and flame propagation.

Konnov's mechanism was tested by Duynslaegher et al. [80] for stabilized flame experiments of ammonia–oxygen–hydrogen mixtures. They found that the model overestimated the mole fraction profile of NH₂ and underestimated the N₂O one. Therefore Duynslaegher et al. [80] implemented new rate constants for the reactions involving nitrous oxide and amidogen radical. As NH₂ is the key intermediate species in the oxidation of ammonia, the improvement of NH₂ radical predictions lead to a significant improvement on other radicals and species profiles.

Mendiara and Glarborg [81] developed a kinetic model for NH₃ oxidation, based on the Tian mechanism, for the oxy-fuel combustion of CH₄/NH₃, conducting experimental tests in a laminar flow reactor in the temperatures range 973-1773K, under atmospheric pressure and equivalence ratios between 0.13 and 0.55. They identified the formation of HNO *via* NH₂+O as important path for NO production.

The high pressure oxidation of ammonia was studied by Mathieu and Petersen [82]. The mechanism was established for ammonia oxidation from shock tube experiments under high temperatures (1560–2455K) and high pressures (around 0.14, 1.1, and 3.0MPa) conditions.

Other detailed chemical models, originally developed for hydrocarbon or syngas, can be potentially used for ammonia oxidation.

For instance, the GRI Mech 3.0 mechanism [83] includes the formation of NO_x and reburn chemistry and it was demonstrated to provide satisfactory results for the prediction of ammonia-doped methane/air flames.

Recently, Zhang et. al. [84] developed a detailed kinetic mechanism for hydrogen/NO_x and syngas/NO_x systems. The mechanism was tested for several conditions and experimental facilities, like shock tube ignition delay times, species prediction in the jet-stirred reactors (JSR), and flow reactors (FR), nonetheless without taking into account

NH₃ system for model validation. In their analysis, they found out that different mechanisms from literature have different outcomes and are only suited for specific systems.

The same conclusion was given by Xiao et al. [85], that studied ammonia/hydrogen blends with various kinetic models, suggesting that all these mechanisms present considerable discrepancies between experimental results at various conditions.

The reason for such inconsistencies is that most of the kinetic models are developed for specific operating conditions (equivalence ratios, mixtures composition and dilution, pressures, temperature, etc). Each condition involves specific reaction pathways, making critical the development of a comprehensive kinetic mechanisms, capable of capturing accurately the complex behavior of ammonia combustion.

Therefore, fundamental studies are necessary to understand the oxidation of ammonia. The deep comprehension of the process must rely on detailed reaction models validated against traditional and non-conventional combustion conditions. In order to assist this process, several experimental data are required, spanning different types of practical and ideal systems and a wide range of operative conditions.

2.1.3. The potential impact of heterogeneous reactions on the gas-phase oxidation of ammonia

A significant part of experimental data concerning nitrogen chemistry in combustion, in particular NO_x formation and reduction, is obtained in quartz flow reactors, due to the chemical inertia of quartz in combustion processes [86]. Radical recombination on quartz surface was extensively investigated in literature for H, OH, O, HO₂ and N-radicals. Based on the experimental evidences, in general the loss of radicals in quartz can be neglected at temperatures relevant for combustion conditions [87].

Nevertheless, some nitrogen species, in particular ammonia, are known to adsorb and decompose on quartz surface. Indeed, due to slow ammonia homogeneous reactions, heterogeneous interaction with surfaces can be relevant, thus the interpretation of data must be careful.

Several works deal with the interaction between ammonia and solid surfaces [88–91]. Tsyganenko et al. [91] studied the formation of surface species arising from the adsorption of ammonia on oxide surfaces. They suggested that the way ammonia interacts with solid oxides depends on the temperature and on the presence of hydroxyl group on oxide surface. They mentioned three types of retention:

- 1. Formation of hydrogen-bonding between the nitrogen atom of ammonia and the hydrogen atom of the hydroxyl group on oxide surface;
- 2. Formation of hydrogen-bonding between the hydrogen atom of ammonia and the oxygen atom of the solid oxide;
- 3. Lewis interaction among ammonia and electron-deficient metal atom of the oxide.

The system temperature can boost the dehydroxylation of the material surface, thus influencing the type of surface interaction. Tsyganenko et al. [91] found different spectra of ammonia adsorbed on SiO₂ surfaces while heating the sample up to 700-800°C. At higher temperatures, they observed the spectrum of surface NH₂ group, not revealed at low temperatures. They found analogues results studying the spectrum of ammonia adsorbed on Al₂O₃.

Glarborg et al. [87] studied the potential impact of these surface interactions on the thermal $DeNO_x$ process in a flow reactor. They described the heterogeneous decomposition of ammonia by a single-site ammonia adsorption step. They modeled the experimental NH₃ and NO profiles obtained by Hulgaard and Dam-Johansen [92] in a plug flow, with and without the surface chemistry. They claimed that heterogeneous reactions are negligible for the analyzed conditions, due to small reactor surface/volume (S/V) ratio [87]. These results were also confirmed by Lion and Benn [93] studying the thermal DeNO_x. They concluded that surface decomposition of NH₃ was not important for the SNCR process in systems with low S/V ratio.

In addition, Glarborg et al. [87] argued that the presence of H_2O may inhibit the surface decomposition of ammonia because water can interact with solid oxides by both molecular and dissociative adsorptions, depending on the temperature [94–96]. In literature, it is also documented that, in flow reactor experiments, the water vapor alters the surface conditions, thus the silica surface is less active [62].

Kijlstra et al. [94] studied the effect of water in Selective Catalytic Reduction (SCR) processes and they suggested that water can inhibit or deactivate both the catalyst and the γ -Al₂O₃ support reactivity.

Despite the literature is plenty of works dealing with ammonia heterogeneous chemistry on surfaces, for the most they are relative to SCR catalysts (i.e. metals and metals oxides, noble metals, zeolite), while few and sparse information are available for quartz or alumina surfaces, usually used as catalyst supports [91,94].

2.2. Third-body molecular reactions under MILD conditions: the plausible role of ammonia as collider

The definition of fuel oxidation chemistry under MILD conditions is challenging since it occurs at temperatures lower than traditional flames and under vitiated conditions [12,15]. This, in turn, emphasizes the role of third-molecular reactions in virtue of relatively low working temperatures and the massive presence of "strong" colliders, namely H₂O and CO₂ [12,15]. Steam and carbon dioxides are tri-atoms molecules classified as "strong" colliders due to their higher collisional efficiencies with respect to those usually assigned to N₂ or Ar in fuel detailed kinetic mechanisms. In the case of the most important reaction for fuel oxidation at relatively low temperatures, $H+O_2+M=HO_2+M$ [15,97–102], carbon dioxide and water, in detailed kinetic mechanisms, conventionally have a collisional efficiency 3-5 and up to 20 times larger than that of other atomic and diatomic baths,

respectively [98,103]. Recently, Sabia and de Joannon [15] have experimentally characterized the oxidation of H₂-O₂ diluting the mixtures in N₂, CO₂ and partially in H₂O, to put in evidence the effects of such species on hydrogen combustion features for operating conditions within the hydrogen third-explosion limits. They showed that both dilution in CO₂ and H₂O considerably decrease mixtures reactivity, with respect to the baseline case of dilution in N₂, shifting stable combustion region towards higher preheating temperatures, in agreement with many other literature evidences, reported in [12,13,15].

The collisional efficiency C_M is defined as the ratio between the rate constant for the lowpressure limit when *M* is bath gas ($K_{0,M}$), with respect to the one associated to a reference gas (commonly Ar or N₂) ($K_{0,Ar \text{ or } N_2}$):

$$C_M = \frac{K_{0,M}}{K_{0,Ar \text{ or } N2}}$$

Despite the constant parameters in the Arrhenius law allow for a relatively simple description of chemical kinetics and can be straightforwardly derived from experimental results, the collisional efficiencies hide the real nature of molecule interactions during chemical reactions giving a macroscopic description of the reactive process. As a consequence, the approach used for modeling combustion kinetics, extremely effective for standard fuels and standard combustion processes, can show significant weaknesses when the dependence of these parameters on molecule characteristics or temperature becomes relevant and significant deviations from the usual parameters values can occur. More complex theories define reaction rates from a microscopic point of view and the parameters that are constant in Arrhenius equation become function of several quantities. For example, collisional theories describe the dynamics of collisions among molecules through the probability of collisions, the nature of collisions (anelastic, elastic scattering), the orientation of molecules during a collision, along with the intramolecular exchange of energies (vibrational, rotational), with the implementation of functions more and more complex as arriving to the real nature of chemical kinetics involved in combustion systems. In this case, the rate constants K(T) for elementary reactions are specified according to the equation:

$$K(T) = \rho Z e^{-\frac{\Delta E}{RT}}$$

Where:

 ρ = steric factor or probability, it represents the probability that molecules interact with a correct mutual orientation.

Z =collisional frequency, (m⁻³s⁻¹)

 ΔE = minimum kinetic energy required for molecular collision to lead to the reaction. For bimolecular reactions, the collisional frequency (Z) has the form of:

$$Z = \sigma_{ab} \sqrt{\frac{8K_BT}{\pi\mu_{ab}}}$$

where:

 σ_{ab} = collisional cross-section, the area two molecules (A and B) collide each other, (m²)

 K_B = Boltzmann's constant, (m² Kg s⁻² K)

 μ_{ab} = reduced mass (m) of reactants A and B, $m_a m_b / (m_a + m_b)$.

The outstanding parameter to be determined here is the collisional cross-section σ_{ab} . The most simple definition is $\sigma_{ab} = \pi(r_a + r_b)$, where r_a and r_b are the molecular radius of molecule A and B, respectively.

In more advanced theories, the collisional cross-section is derived from the Lennard-Jones potential [104–107], that mainly considers "hard spheres" molecules can attract each other (Wan der Walls forces $\left(\frac{\sigma}{r}\right)^6$) and repulse at shorter distance (Pauli repulsion forces $\left(\frac{\sigma}{r}\right)^{12}$):

$$V(r) = 4\varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right)$$

Here ε is the depth of the potential well and σ is the molecules collisional cross-section calculated at V(r) = 0.

More accurate potentials take into account the various atomic-molecular interactions. In this case, the potential in its general form can be written as:

$$V(r) \propto -\frac{1}{r^n}$$

where *n* depends on interaction typology. In the case of dipole-dipole interaction, the attractive term $V(r) = -\frac{\sigma}{r^3}$ has to be considered, with a consequent increase of the collisional cross-section. In addition, for large molecules, the hypothesis of "hard spheres" cannot be applied, thus also molecules orientation has to be considered during molecule collisions. The Stock-Mayer potential considers both the molecule dipole moment and molecular orientation per collision:

$$V(r) = 4\varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 - \delta \left(\frac{\sigma}{r}\right)^3 \right)$$

where δ is a function that describes the angular dependence of the dipole-dipole interaction energy.

The potential can be further specified with additional terms, identified as dispersion forces $(V(r) \propto -1/r^6)$, with the same order of magnitude of van der Walls forces. Dispersion forces include several contributions as the attractive potential associated to oscillating nature of dipoles or the dipole-induced dipole interaction. The last one requires a permanent dipole in one of the two interacting molecules (species A). This attractive contribution can be expressed in the form:

$$V_{ind}(r) \propto rac{\mu_a^2 \alpha_b}{r^6}$$

where α_b is the species polarizability of the molecule with no permanent dipole (species B).

It is very interesting to give at a glance the characteristic of relevant molecules and radicals involved in combustion systems and herein of interest, such as the 3D structure,

the molecule cross section, the dipole moment and polarizability, which are reported in Figure 3.

	3D structure	σ [Å]	μ _D [D]	α [ų]
Ar		3.330	0	1.642
N ₂	F	3.621	0	1.750
CO ₂	F	3.763	0	2.65
H ₂ O		2.605	1.847	1.450
NH ₃		2.920	1.472	2.81
HO ₂	.	3.458	2.09	1.970

Figure 3. Structure, molecule cross section, dipole moment and polarizability of the species of interest.

It is possible to note that CO_2 has a larger cross section with respect to Ar or N₂, with nopermanent dipole moment but it is polarizable (more than Ar or N₂). Many works deal also with the quadrupole nature of CO_2 [108,109]. H₂O has a lower cross section with respect to Ar or N₂, while it exhibits a permanent dipole moment and, at the same time, is polarizable. Considering the relevant role of HO₂ radicals, as for example in the reaction H+O₂+M=HO₂+M, it is worth noting that HO₂ as well has a large cross-section, a large permanent dipole moment and is polarizable (many authors have attributed the high collisional efficiency of water to a very strong polar-polar interaction between HO₂ radicals and H₂O [99,102]).

Even though this information is commonly used to calculate the transport properties (diffusivity, viscosity, thermal conductivity) of species to be used in combustion modeling [105,106,110], they are not considered in the calculation of rate constants within collisional theory.

Recent works tried to address issues related to the dipole-dipole interactions [102,103], with the expression of the collisional frequency equal to:

$$Z \propto (\mu_a \mu_b)^{\frac{2}{3}} (K_b T)^{-\frac{1}{6}} \left(\frac{8\pi}{\mu}\right)^{\frac{1}{2}}$$

where the dipole-dipole interaction is given through the term $(\mu_a \mu_b)^{\frac{1}{3}}$. They claim this expression is valid for molecules with dipole-induced dipole interactions (dispersion forces), but it is more appropriate than the one derived from the simple Lennard-Jones potential. The collisional theories are far from an exhaustive description of all these contributions (dipole-dipole interactions, polarizability, etc.) through the collisional frequency expression. On the other hand, the Arrhenius expression hides all these

contributions in empiric parameters for the definition of the rate constants and by the third-body collisional efficiencies of species.

Based on these considerations, molecular polarity is a very important chemical/physical property in combustion chemistry. In particular, ammonia is a relevant case of a molecule that, having a relatively high polarity and a dipole moment comparable to that of water (as reported in Figure 3), is likely to exhibit a large third-body effect. Its third body effect cannot be ruled out "a priori" in chemical kinetics modelling of ammonia combustion, but it has to be addressed through experimental evidences.

The same considerations can apply to many alternative fuels in the palette of new energy carriers.

2.3. Aim of the thesis

The literature survey revealed that ammonia oxidation process is still far from being fully understood. Although the behavior of this molecule has been extensively studied under conditions relevant to the $DeNO_x$ process, it is evident that there is no kinetic mechanism in literature capable of describing its main combustion features. Such critical issues may become even more relevant for unconventional combustion processes, such as MILD combustion, where high dilution levels and relatively low temperatures promote alternative kinetic pathways, in which ter-molecular reactions play a key role.

For these reasons, the understanding of each aspect of ammonia combustion and the development of a robust and reliable mechanism that can simulate experimental data are of the highest importance.

Most of the available kinetic models have been validated against experimental data for ammonia/air mixtures at high temperature, while ammonia speciation has been studied at high temperature for very high dilution level (>99%). Therefore, there is a need of optimal experiments in order to restrict uncertainties for low temperatures and lower dilution conditions.

Given this background, the objective of the current thesis was to investigate the oxidation process of ammonia mixtures in a model reactor. In particular, the experimental tests were carried out in a Jet Stirred Flow Reactor. This system allows the quantification of all major and minor species concentrations as a function of the system parameters, as well as the identification of oxidation regimes, providing important targets for the validation and optimization of kinetic mechanisms.

The experiments were performed for several inlet temperatures, equivalence ratios, dilution level and for different bath gases, at atmospheric pressure. The effect of doping ammonia mixtures with hydrogen and nitrogen oxide was even investigated. The study focused on low-intermediate temperature conditions, that are of practical interest to diluted combustion applications. The plausible role of ammonia as third-body species in three body reactions was also taken into account through an indirect evaluation of the ammonia effects on the H₂-O₂ oxidation.

The detailed list of the explored operating conditions is provided case-by-case in the Chapter 1.

The experimental campaign revealed new insights into ammonia oxidation process and provided relevant constraints for models validations.

Following the experimental study, the performance of updated kinetic models in predicting the data was tested. Therefore, numerical analyses were performed in order to understand the main reaction pathways and identify the possible sources of disagreement between the models prediction and experimental data.

On the basis of all the experimental findings and numerical analyses, a final effort to model ammonia oxidation features was made, improving the performance of an available kinetic mechanism, by updating it with more accurate rate constants and tuning the kinetic parameters of the most sensitive reactions.

3. EXPERIMENTAL AND NUMERICAL TOOLS

3.1. Jet Stirred Flow Reactor

The Jet-Stirred Flow Reactor (JSFR) belongs to the categories of Continuous Stirred Flow Reactors (CSTR) [86,111]. A premixed mixture is continuously fed within the reactor volume, where reactions take place. Ideally, fresh reactants perfectly mix with outlet products defining a uniform system with no spatial gradients of mixture intensive and extensive properties within the entire reactor volume. The homogeneous condition imposes that the composition of the gas inside the reactor and the outlet ones are equal. This configuration allows for the characterization of chemical processes as a function of system parameters (i.e. residence time, mixture composition, pressure, pre-heating temperature) also for processes characterized by small characteristic time scales (combustion processes), given that the "perfect mixing condition" is respected (i.e. characteristic mixing time shorter than chemical ones).

These operating conditions allow to describe the system behaviors by simple mass and energy balances as a function of the time, while neglecting the fluid-dynamics of the process. These aspects pose the basis for the possibility to implement complex chemistries in dedicated software, in order to develop detailed kinetic mechanisms. The use of CSTR poses several advantages:

- 1. It allows to study the detailed chemical kinetics of oxidation/pyrolysis processes and the formation chemistry of pollutants as a function of system external parameters (i.e. mixture composition, pressure, pre-heating temperature). In virtue of the "homogeneous" condition, analytical techniques (chromatography, mass spectrometry) for the identification and the quantification of the species in the gas phase can be easily implemented at the reactor outlet, gaining information relative to the reactor state.
- 2. It allows for the identification of combustion regimes, bi/multi-stability features such as the transitions from ignition and extinction limits with respect to external parameters or thermo-kinetic instabilities, with the possibility to preserve such phenomenologies in time because of the "continuous flowing" condition. Fast time response thermocouples can be used to characterize instabilities in terms of oscillation shapes and frequencies.
- 3. It allows to simply control the inner reactor conditions to the case-study by adjusting the system external parameters, thus providing the opportunity to deeply resolve the oxidation/pyrolytic process. The tuning of system external parameters, as mixture dilution levels or the averaged residence times, can easily allow to elongate the characteristic chemical times as well as the heat release rate defining "quasi-isothermal" conditions, thus fixing and easily controlling the reactor temperature to the desired value.

In case of JSFRs, the mixing is realized by injecting turbulent premixed jets into a chamber designed to maximize stirring by jets interaction, swirl flow and turbulence

intensity. The entrainment of the burning mixture causes sufficient recirculation to establish a uniform concentration and temperature throughout the reactor.

The rules for the design of spherical jet-stirred reactors were suggested by Matras and Villermaux [112,113]. The fresh gases enter the reactor through an injection cross located at the center of the sphere. It is composed of four nozzles providing jets that ensure the mixing of the gas phase.

The behavior of JSFRs is described by two global equations relative to mass and energy balances as a function the time. In order to define the problem, several conditions should be declared:

- 1. Geometry of the reactor (volume, surface);
- 2. Inlet conditions (mixture composition, inlet temperature, mixture averaged residence times, pressure);
- 3. Definition of the "adiabaticity" condition of the reactor.

The first point concerns the identification of reactor volume and surface. Modelers do not need the identification of the geometry of the system, since the declaration of reactor volume and surface is sufficient to describe convective properties of the inlet flow (i.e. averaged residence time) and heat exchange phenomena, provided that parameters required at point 2) and 3) are given. In any case, the common shapes of JSFR is a sphere, to avoid the formation of "dead" volumes within the reactor and guarantee system uniformity.

The definition of mixture inlet composition implies the declaration of fuels, fuel/oxygen ratio (for instance mixture equivalence ratio), diluent specification and mixture dilution level. In addition, mass flow rates, or alternatively the mixture averaged residence time have to be declared for the description of the convective term of mass balance equation. The experimental pressure has to be provided as well.

The sensible enthalpy equation implies the declaration of the reactor adiabaticity, with the identification of "adiabatic", "non-adiabatic" or isothermal conditions. In the case of "non-adiabatic" conditions, the global heat transfer coefficient has to be provided. The declaration of isothermal conditions implies that energy balances can be neglected.

The definition of parameters required in these points is sufficient to model the behavior of a JSFR.

The combustion process occurring in the reactor can be described by monitoring reactor temperature at steady or unsteady states, along with species concentration measurable by advanced chemical or diagnostic techniques.

In this thesis, the oxidation of ammonia mixtures was studied in a spherical JSFR, with a volume of 113 cm³. The experimental facility was provided by the National Research Council (CNR-Napoli, Italy). The reactor is made in quartz to prevent catalytic reactions. A picture of the reactor is reported in Figure 4.

A main flow (oxygen and diluent) and a secondary flow (fuel and diluent) are fed separately to the reactor through two different quartz tubes. The streams mix in a premixing chamber just before entering the reactor, through four nozzles of 1 mm diameter located at its center.

The reactor and the gas feeding lines are located within two semi-cylindrical electrically heated ceramic fiber ovens. The temperature gradients within the ovens are minimized by a recirculating air system.

The flow rates of gases from gas-cylinders are measured and regulated by digital thermal mass flow controllers supplied by BronkHorst High-Tech with a high accuracy ($\pm 0.5\%$). For water supply, the system is equipped with an evaporator system (CEM BronkHorst Hith Tech) and a liquid mass flow controller. The controllers are connected to a computer and managed by sub-routines developed in Labview. The pressure is kept constant at nearly atmospheric pressure by means of a needle valve on the exhaust line.



Figure 4. Picture of the JSFR used for the experimental tests.

3.2. Laminar Flow Reactors

In order to investigate in advance the possible occurrence of heterogeneous reactions during ammonia oxidation, preliminary experimental tests were carried out in two laminar flow reactors (LFRs) made of different material: quartz and alumina.

The LFRs are tubular reactors, 1 m long with an ID equal to 0.008 m, and an OD of 0.012 m. The mixture velocity was fixed equal to 3 m/s to ensure the condition $D/(\mu L)<0.01$ to neglect dispersion effects and assume a plug flow reactor behavior [111].

The reactors are displaced symmetrically within two semi-cylindrical electrically heated ceramic fiber ovens with a heating length of 0.6 m. The temperature within the oven is monitored by five thermocouples (type N, with a precision of $\pm 0.75\%$) equi-distributed along the height of the heated part of reactors and located close to their external surface. Air is insufflated within the ovens to homogenize the temperature, thus resulting in a maximum difference between the inlet and outlet of the LFRs of about 10 K under non-reactive conditions.

The averaged value of the five thermocouples was chosen as the reference temperature (T_{ref}) for the experimental tests. Another thermocouple (type N) is positioned inside each reactor at the end of the heated part as indicator of system reactivity.

It must be underlined that the S/V ratio for the LFRs is approximatively 5 times greater than the one of the JSFR, thus the effect of heterogeneous reactions is expected to be enhanced.

A picture of the LFRs system is reported in Figure 5.



Figure 5. Picture of the LFRs used for the evaluation of NH₃-surface interaction.

It must be highlighted that the data obtained with the LFRs cannot be straightforwardly used for modeling activities, because T_{ref} is not indicative of the real thermal state of the reactive mixtures. The experimental campaign in such a facility was just meant to give important information relatively to the interaction of ammonia homogeneous/heterogeneous chemistry with different materials. Indeed, since the reactors work under the same operative conditions, any difference in the experimental species profiles has to be correlate to the different surface materials, thus denouncing the occurrence of heterogeneous reactions.

3.3. Measurements methodology

For both the JSFR and LFRs systems, the exhaust gas composition is analyzed by several tools. A period of time (about 5 min) was waited to stabilize the flow after the fuel injection and before the chemical analyses. The exhaust gases temperature is maintained at about 350K, by means of a heating system, to prevent water condensation (considering the water maximum vapor pressure in the exhausted flow) and subsequently ammonia solubilization. A FTIR analyzer Sick GME700 is installed for NH₃ and H₂O measurements. The maximum NH₃ detectable value is 0.4% with a relative error of 2-4% with respect to the instrument full-scale. Afterwards, the water content is retained by a silica gel trap.

The dry flow is analyzed through a gas-chromatograph (Agilent 3000) to detect O_2 , H_2 and N_2 , while NO_x concentration is measured by an online analyzer (TESTO 350). The maximum relative errors for O_2 and H_2 species are around $\pm 3\%$ (molar fraction). The estimated error for NO_x emissions is ± 2 ppm in the range of 0-99.9 ppm, and $\pm 5\%$ in the range of 100-500 ppm.

In the case of mixture diluted in water vapor, since water is condensed prior to analysis, the measured concentrations are higher than the real ones. Therefore, to compare the results obtained in the case of mixtures diluted in water with the other cases (in which, in turn, concentrations are reported on a dry basis), the volumetric percentage of a generic species was scaled on the basis of H_2O content according to the equation:

$$x_{species} = \frac{x_{dry,measured} \cdot (100 - x_{H_2O}^{dilution})}{100}$$

Experiments were daily repeated at least three times under the same operating conditions and verified also in different days.

To monitor the temperature during gas reactions, an unshielded R-type thermocouple (0.1mm tip size) with a fast response time (less than 30 ms) and a precision of $\pm 0.25\%$ was used. In order to detect temperature oscillations, a National Instruments module capable of acquiring 95 samples per second for each channel was used.

A large set of experimental operative conditions was explored to investigate the combustion of NH₃ mixtures. Specific details are provided in the Chapter 4, case by case.

3.4. Evaluation of surface effects

The interpretation of data on the oxidation of ammonia in quartz reactors must be careful, because, due to slow ammonia homogeneous reactions, heterogeneous interaction with surfaces can be relevant (as discussed in the Paragraph 2.1.3), thus introducing uncertainties in the evaluation of the gas phase reactivity.

Therefore, before undertaking any experimental study on NH₃ oxidation, the evaluation of such heterogeneous interactions under the operative conditions of concern is mandatory.
The approach to the problem was twofold.

First, an experimental study was performed for stoichiometric NH₃/O₂ mixtures diluted in Ar at 86% and Ar(84.5%)-H₂O(1.5%), at fixed pressure (p=1.2 atm) and residence time (τ =0.25s). A low concentration of water was used to passivate the quartz surface limiting its potential interaction with ammonia oxidation chemistry. Indeed, literature on NH₃surface interactions suggests that water can inhibit or limit ammonia adsorption on the surface active sites (as reported in the Paragraph 2.1.3).

Second, the analyses proceeded throughout experimental tests in the LFRs, to value the heterogeneous effects with different materials.

For the LFRs tests, the stoichiometric $NH_3/O_2/Ar$ mixture diluted at 86% was considered, at atmospheric pressure and constant velocity (v=3m/s).

The operative conditions for both the systems are summarized in Table 2.

Conditions	Range
Inlet temperature (Tin)	900-1350 K
Equivalence ratio (Φ)	1
Residence time (τ) or velocity (v)	τ=0.25 s (JSFR), v=3m/s (LFRs)
Pressure	1.2 atm
Diluent (d)	86% Ar, 84.5% Ar - 1.5% H ₂ O

Table 2. Experimental operative conditions for the evaluation of surface effects, for the JSFR and LFRs facilities.

The experimental results for the NH₃ oxidation in the JSFR are presented in Figure 6. For both the mixtures, the O₂ conversion (Figure 6a, grey symbols) is negligible for T_{in} <1200 K, then it starts to increase with T_{in} , and for T_{in} >1250 K it is complete. The temperature profile is consistent with the O₂ trend. Figure 6b is relative to the H₂ concentration. It is possible to see that for both the mixtures, H₂ concentration increases with T_{in} up to a relative maximum value of about 0.18% for T_{in} =1130 K, then for 1130< T_{in} <1250 K it decreases down to the minimum (0.085%). For T_{in} =1250 K, it reaches its maximum concentration then it is consumed.

The N_2 concentration, coming from ammonia reactions, increases monotonically as a function of the inlet temperature (Figure 6c). The similarity of the key species profiles for the two analyzed mixtures suggests that NH_3 reactivity is not affected by surface interactions, for the operative conditions here investigated (mixture composition, averaged residence time and JSFR surface/volume ratio).

Small differences can be observed for the NO profiles (Figure 6d). For the mixture without H₂O, NO concentration increases as a function of the temperature for T_{in} <1130 K, then it is almost constant for 1130< T_{in} <1250 K. For higher temperatures, it abruptly rises up to 160 ppm.

In presence of H_2O , NO concentration monotonically increases as a function of T_{in} . In general, values are very similar for both the mixtures in the considered temperature range,

with small differences within the intermediate temperature range. Indeed, NO concentrations are slightly greater for the Ar diluted mixture with respect to the Ar-H₂O diluted one. However, these differences consist of no more than 5-6 ppm (value close to the instrument detection limit) and are restricted to the intermediate temperature range.



Figure 6. ΔT , O_2 , H_2 , N_2 , NO experimental profiles as a function of T_{in} , for the oxidation of stoichiometric NH₃/O₂/Ar (d=86%) and NH₃/O₂/Ar/H₂O (d=84.3% Ar-1.7% H₂O) mixtures, at fixed p=1.2 atm and $\tau=0.25$ s, in JSFR

The experimental results presented in Figure 7 refer to the oxidation of a stoichiometric $NH_3/O_2/Ar$ mixture in two LFRs.

Given the symmetry of the system, the two tubular reactors can be considered to work under the same operative conditions (as verified by the temperature measured by the two thermocouples positioned internally at the end of the two reactors).

The influence of the materials is evaluated by a comparison of key species as a function of a reference temperature (T_{ref}). It is defined as the averaged value of five thermocouples equi-displaced along the external wall of the tubular flow reactors. For this reason, T_{ref} is not representative of the temperature within the reactors.

 O_2 profiles (Figure 7a) are very similar for both reactors. Its concentration remains equal to the inlet one up to 1200 K, then it decreases to 0. Similarly, H₂ profiles (Figure 7b) are approximately coincident for both reactors: for T_{ref}<1120 K H₂ concentration is equal to zero, then, for higher T_{ref} it increases.



Figure 7. O_2 , H_2 , NO experimental profiles as a function of T_{ref} , for the oxidation of stoichiometric NH₃/O₂/Ar (d=86%) mixture at atmospheric pressure and v=3 m/s, in LFRs.

In the quartz reactor, for $T_{ref} < 960$ K NO concentration (Figure 7c) increases until a relative maximum at around 30 ppm. For $960 < T_{ref} < 1250$ K NO profile decreases down to 10 ppm, while for the higher temperatures, NO concentration abruptly rises to 1720 ppm.

Within the alumina reactor a similar NO trend can be observed. For T_{ref} <960 K, NO concentration increases as a function of the temperature, then, for an intermediate temperature range (960< T_{ref} <1100 K) it decreases down to 40 ppm and at higher temperatures (T_{ref} >1100 K) it increases again to a maximum detected value of about 1800 ppm.

These results confirm the ones obtained in the JSFR. In fact, the O_2 and H_2 concentrations plotted with respect to T_{ref} are independent of the material, because they show the same trends and values for both the reactors, while NO profiles exhibit negligible differences within the low-intermediate temperature regime. At higher temperatures, NO concentrations overlap, since NH₃ homogeneous reactions become relatively fast, thus heterogeneous reactions are less important.

Therefore, NH₃ oxidation is likely to not be affected by surface interactions in the JSFR. The surface effect on the NO profiles are enhanced in the LFRs with respect to the JSFR, due to the greater S/V ratio. Additionally, the differences between the NO concentrations

for the alumina and quartz reactors could be ascribed also to the different acidic properties of the materials.

3.5. Computational approach

In this work, several detailed kinetic mechanisms, validated for a wide range of conditions, were tested to check their validity against experimental data obtained in the JSFR.

Hereafter, each mechanism is identified by the name of the first author of the research group. The characteristics of each mechanism, along with the corresponding validating conditions, are summarized in Table 3.

Glarborg et al.'s mechanism [62] was developed to predict the chemical kinetics that control NO_x formations and reductions in oxidation processes. In their scheme, NH_3 submechanism was based on the work by Klippenstein et al. [114] and validated against experimental data by Bian et al. [115] on low-pressure (35 Torr) flame, for near equimolar ammonia-oxygen mixtures. The mechanism was tested also for NH_3 ignition delay time prediction against the experimental data by Mathieu and Petersen [82].

The kinetic mechanism by Song et al. [116] was validated against ammonia ignition delay time. Experiments were performed in a laminar flow reactor at high pressure (30 and 100 bar) and low temperatures (450-925 K). The reaction pathway $NH_3 \rightarrow NH_2 \rightarrow H_2NO \rightarrow HNO \rightarrow N2$ was recognized as the main oxidation mechanisms at high pressures.

Kinetic mechanism	Reactions	Species	Validation details
Konnov [117]	286	36	Ammonia pyrolysis in shock waves, T=2200-2800 K, p=1 atm
Glarborg et al. [62]	1397	151	Equimolar NH ₃ -O ₂ -Ar flame, p=35 Torr
Song et al. [116]	204	32	Laminar flow reactor, ¢≤1; T=450-900 K; p=30, 100 atm
Nakamura et al. [118]	232	38	Weak flames, \$\phi=0.8, 1.0, 1.2; T<1400 K; p=1 atm
Otomo et al. [52]	213	33	Laminar flame speed of NH ₃ /H ₂ /air, ϕ =0.7-1.3, p=1, 3, 5 atm
Shrestha et al. [119]	1090	125	Various conditions and several facilities (tubular reactors, jet stirred reactors, shock tubes)
Zhang et al. [84]	251	44	Various conditions and several facilities (tubular reactors, jet stirred reactors, shock tubes)

 Table 3. Detailed kinetic mechanisms used for simulations.

Zhang et al. [84] developed a detailed kinetic mechanism to describe the oxidation and pyrolysis of H_2/NO_x and syngas/NO system. The mechanism was validated against

several data sets (ignition delay times, flame speed measurements, temperature and species profiles) from various experimental facilities (tubular reactors, jet stirred reactors, shock tubes). The reactions related to NH₃ chemistry were taken from the work of Mathieu and Petersen [82] and modified based on the work of Dagaut et al. [60].

The mechanism by Nakamura et al. [118] was validated against ammonia/air mixtures weak flames at different equivalence ratios (0.8, 1.0, 1.2), under atmospheric pressure and temperature lower than 1400K, in a micro flow reactor. The model was developed from Miller and Bowman's mechanism [120], including N_2H_x chemistry from Konnov's scheme [117]. N_2H_x sub-mechanism was developed by Konnov [117] and Konnov and De Ruyck [121,122] studying ammonia and hydrazine decomposition.

The Otomo et al.'s kinetic mechanism [52] was developed from the work by Song et al. [46] and the chemistry related to NH_2 , HNO and N_2H_2 was modified. The model was validated against laminar flame speed data of $NH_3/H_2/air$ mixtures as a function of the mixture equivalence ratio.

The comparison between the models predictions and the experimental profiles allowed to identify performance and, then, inconsistencies in the prediction of ammonia mixtures oxidation under low-intermediate temperature and diluted conditions.

The simulations were carried out using the PSR code of ChemKin PRO [123]. The system was modeled as isothermal when high dilution levels are used, as the heat release from the oxidation process can be neglected. Differently, for lower dilution levels, the system was modeled as non-adiabatic. The global heat transfer coefficient (U) was experimentally calculated on the basis of a heat balance equation under non-reactive conditions. The mathematical balance is:

 $\dot{m}c_{p,mix}(T_{in} - T_{out}) = AU(T_{ext} - T_{out})$ where:

- \dot{m} is the mass flow rate;
- $c_{p,mix}$ is the specific heat capacity of the mixture;
- *A* is the reactor surface;
- $(T_{in} T_{out})$ is the difference between the inlet temperature and the outlet temperature;
- $(T_{ext} T_{out})$ is the difference between the external temperature, i.e. the oven one, and the outlet temperature.

The inner heat transfer coefficient was verified also by means of a Nusselt correlation, proposed by Reverchon [124] for JSFRs:

$$Nu = \frac{UD}{k} = 0.89Re^{0.683}Pr^{1/3}$$

where:

- k is the thermal conductivity of the gas mixture
- *D* is the reactor internal diameter.
- $Pr = \mu c_p/k$ is the Prandtl number (μ is the dynamic viscosity).
- $Re = \rho v d/\mu$ is the Reynolds number evaluated for nozzles (d nozzle diameter)

This coefficient was then verified also by means of CHEMKIN PRO. Simulations for reactive conditions well predicted the final steady states of NH₃/O₂ mixtures at high temperatures (where the thermodynamic equilibrium is reached) for different operative conditions.

In this context, it is worth declaring that a variation of the heat transfer value within uncertainties values would slightly change the temperature (within the same uncertainties of thermocouple measurements), while would not change the concentrations of species (less sensible to few temperature degree difference).

Specifications of the reactor and the system parameters were the same as those of the experimental ones. The wall temperature is assumed equal to the inlet temperature.

Detailed kinetic studies were carried out following the numerical simulations. The flux diagrams, Reaction Rates (RRs) and sensitivity analyses were used to identify the controlling reaction pathways for the analyzed operative conditions. Moreover, these analytical tools allowed to recognize critical issues and discrepancies among the mechanisms, in order to outline possible sources of disagreement between the model predictions and experimental data.

4. EXPERIMENTAL RESULTS AND NUMERICAL ANALYSES

The analysis of the ammonia oxidation under low-intermediate temperatures and diluted conditions has been challenging and gradually revealed interesting and unexpected results. After having verified the negligible role of NH₃-surface interactions under the conditions of interest, an exploratory experimental campaign was carried out, that highlighted peculiar features and different combustion behaviors of NH₃/O₂ mixtures, dependent on the working temperature and mixture stoichiometry.

The effort to understand such experimental results through numerical analyses with available detailed kinetic mechanisms has, in turn, brought to the light serious inconsistency between data and numerical predictions and, more interestingly, a diverse description of the low-temperature oxidation chemistry.

Such results have suggested the successive steps.

Firstly, a comprehensive experimental study was performed in order to characterize the ammonia oxidation regimes and its transitional behaviors, as a function of the system parameters. Contextually, numerical simulations and kinetic analyses have been performed, in order to identify the most important reactions and their effects on the combustion characteristics.

Apart of the aforesaid inconsistency, this study has highlighted the key role of recombination and decomposition reactions for low temperatures, as well as the importance of the $DeNO_x$ reactions for intermediate ones.

Therefore, as second step, the interaction between NH₃ and NO has been investigated to evaluate the role of the DeNO_x process on NH₃ oxidation.

Subsequently, ammonia thermal decomposition has been explored, in order to assess its impact on the oxidation process.

Hence, the oxidation of NH₃-H₂ mixtures has been studied. Although the initial purpose of such analyses was to investigate the enhancing role of H₂ under MILD operative conditions and its effect on NH₃ oxidation regimes, this experimental campaign has disclosed a peculiar mutual inhibiting interaction of these fuels for low temperatures, thus revealing another important feature of NH₃: its role as strong collider in third-molecular reactions, not contemplated by the considered mechanisms.

Piece by piece, the experimental results reported in this chapter contain relevant information about the combustion process of NH_3 under non-conventional conditions and, in addition, provide important constraints for models validation.

The kinetic analyses, contextually reported for each experimental campaign, aim at identifying the most important reactions and quantifying the effects of these reactions on the combustion characteristics. Following, the main outcomes from the experimental and kinetic studies are summarized and possible sources of disagreement between the model predictions and experimental data were outlined.

Based on this analysis, a final effort to model ammonia oxidation features was made, improving the performance of an available kinetic mechanism, by updating it with more accurate rate constants and tuning the kinetic parameters of the most sensitive reactions.

An overview of the experimental and numerical work is provided as flow chart in the Figure 8.



Figure 8. Schematic description of the experimental and numerical studied carried out in this *PhD thesis.*

4.1. Ammonia oxidation: Low and High Temperature regimes

The preliminary experimental tests were performed at nearly atmospheric pressure and fixed residence time (τ). The oxidation process was analyzed for mixtures diluted in N₂ keeping constant the dilution level (d), for different equivalence ratios (ϕ) as a function of the inlet temperature (T_{in}).

The equivalence ratio ϕ was defined based on the reaction $4NH_3+3O_2=2N_2+6H_2O$, according to this equation:

$$\phi = \frac{(NH_3/O_2)}{(NH_3/O_2)_{stoich}} = \frac{3}{4}(NH_3/O_2)$$

Conditions	Range
Inlet temperature (Tin)	900-1350 K
Equivalence ratio (Φ)	0.8, 1, 1.2
Dilution level (d)	86%, 99.5% N ₂
Residence time (τ)	0.21 s
Pressure	1.2 atm

The experimental conditions explored in the JSFR facility are summarized in Table 4.

Table 4. Experimental operative conditions for the oxidation of $NH_3/O_2/N_2$ mixtures.

The temperature increment ($\Delta T=T-T_{in}$) and the concentration of key species (O₂, H₂ and NO) are reported as a function of T_{in} in Figure 9.



Figure 9. Experimental ΔT , O_2 , H_2 and NO profiles for lean (ϕ =0.8), stoichiometric and rich (ϕ =1.2) NH₃/O₂ mixtures diluted in N₂ at 86%, at atmospheric pressure and τ =0.21s. (oscillations ϕ =1: 1255-1265K, ϕ =0.8: 1255-1285K).

For all the three ϕ considered, the reactor temperature T_r (Figure 9a) starts increasing for T_{in}>1000K up to 1100K, then it increases with a slower slope. Afterwards, for T_{in}>1225K, the reactor temperature abruptly increases. For T_{in}<1225 K, Δ T is almost independent of the inlet mixture composition, while for higher T_{in}, it strongly depends on it. The maximum temperature increase is related to the stoichiometric condition (Δ T=80K). For the cases ϕ =0.8 and 1, a peculiar oxidation behavior was detected: the temporal evolution of the reactor temperature from the initial value to the steady state conditions occur

through instabilities, namely damped temperature oscillations in time. Such behavior was recorded for $T_{in}=1255-1265K$ at $\phi=1$ and $T_{in}=1255-1285K$ at $\phi=0.8$. The detailed study on the transient evolution of the system temperatures is provided in the Paragraph 4.2. O₂ concentration (Figure 9b) is almost equal to the inlet condition for $T_{in}<1100$ K, then it

starts to decrease, and for T_{in} >1225 K O₂ is almost fully converted in relation to ϕ .

The H₂ profiles (Figure 9c) are coincident for T_{in} <1225 K for all the considered ϕ : they start increasing for T_{in} >1000 K, then they reach a maximum value at T_{in} =1100 K. Afterwards, H₂ concentration reaches a plateau up to T_{in} =1225 K. At higher T_{in} , H₂ trends are strongly dependent on ϕ : at ϕ =0.8 H₂ concentration decreases down to 0 at 1300 K, while for the stoichiometric and fuel-rich mixtures H₂ concentrations increase. In particular, for the stoichiometric condition, H₂ increases up to reach a steady value (about 0.3%), while for ϕ =1.2 it monotonically increases with T_{in}.

NO trends (Figure 9d) are slightly dependent on ϕ for T_{in}<1225 K: NO concentrations increase as a function of T_{in} to a relative maximum value at around 1100 K, then they decrease down to a relative minimum at 1225 K. At higher T_{in}, NO profiles exhibit a stronger dependence on ϕ . At ϕ =1.2, NO concentration reaches a plateau, while for the stoichiometric and fuel-lean mixture NO concentrations increase as a function of T_{in}. The maximum NO production occurs at ϕ =0.8.

The non-monotonic H₂ and NO profiles suggest the existence of three different oxidation regimes, namely: low (T_{in} <1100 K), intermediate (1100< T_{in} <1225 K) and high (T_{in} >1225 K) temperatures (LT, IT, HT respectively). In the low-intermediate temperature regime, the system reactivity is almost independent of the mixture composition.

These results are also consistent with those reported in the Paragraph 3.4 for the oxidation of $NH_3/O_2/Ar$ mixture. Indeed, as for the N₂-diluted mixtures, the NO and H₂ non-monotonic trends reported in Figure 6 confirm the existence of three different kinetic regimes. Additionally, comparing the NO profiles from Figure 6 and Figure 9, it is possible to notice that, despite the NO profiles are not exactly coincident due to the different operative conditions, the concentration values are almost similar, thus it can be stated the NO formation is only ascribable to NH₃ oxidation, in other words the contribution of N₂ as diluent to the NO production is negligible.

The analysis of the effect of ϕ on NH₃ oxidation regimes was extended to a wider range of equivalence ratios. H₂ and NO were considered as marker species. ϕ was changed between 0.6 and 1.4. while keeping constant T_{in} at three fixed values (1100, 1225, 1270 K). The first two temperatures are representative of the shift among the different kinetic regimes previously identified, while the latter of the HT regime.



Figure 10. H_2 and NO profiles as a function of ϕ at fixed T_{in} , at atmospheric pressure, d=86%, $\tau=0.21s$.

For $T_{in}=1100$ K (black triangle), H₂ concentration (Figure 10a) is almost independent of ϕ , since its value is around 0.1% for the all the considered ϕ . For $T_{in}=1225$ K (grey square), H₂ profile is slightly dependent on ϕ , as it increases monotonically with ϕ from 0.06% at $\phi=0.6$ up to 0.16% at $\phi=1.4$. At $T_{in}=1290$ K, H₂ is close to zero for fuel ultralean conditions, and starts increasing monotonically for $\phi>0.8$ up to a value of 0.85% for $\phi=1.4$.

NO profiles (Figure 10b) exhibit similar trends for lower temperatures, since they decrease monotonically as a function of ϕ from 56 ppm down to 33 ppm at T_{in}=1100 K and from 20 ppm down to 13 ppm at T_{in}=1225 K.

A stronger effect of the mixture composition on NO production can be observed at $T_{in}=1290$ K. In fact, NO concentration increases as a function of ϕ to a maximum value of 100 ppm at $\phi=0.7$, then it decreases down to 27 ppm at $\phi=1.1$ and remains constant to 20 ppm for greater ϕ .

The previous results confirm the Low- and Intermediate Temperature regimes are slightly affected by the mixture stoichiometry, whereas the equivalence ratio has a major impact on H₂ and NO production for the HT regime.

The experimental results were modeled using the CHEMKIN PRO software and different kinetic detailed mechanisms [62,84,116–118]. The system was modeled as non-adiabatic with a global heat-transfer coefficient equal to 3.5×10^{-3} cal/(cm² s K). Results are reported in Figure 11, for the stoichiometric NH₃/O₂/N₂ mixture. This choice does not compromise the generality of the discussion, since the mechanisms perform similarly for the fuel-lean and the fuel-rich conditions.

The numerical O₂ profiles (Figure 11a) obtained by Nakamura, Konnov and Glarborg envisage a higher conversion with respect to the experimental data at low-intermediate temperatures and suggest the existence of dynamic regimes (periodic oscillations of temperature and species in time, identified by the dashed lines) within the following temperature ranges: 1120<Tin<1300 K, 1150<Tin<1300 K, 1200<Tin<1250 K respectively.



Figure 11. Comparison between experimental profiles and numerical prediction for the stoichiometric NH₃/O₂/N₂ mixture.

Song and Zhang mechanisms predict an overall lower reactivity with respect to experimental evidences and numerical predictions by the other schemes, as O_2 concentration are greater in the same temperature range. In addition, no temperature oscillations were obtained by the Song mechanism. At high temperatures, the experimental O_2 profile is satisfactory reproduced by Song, Glarborg and Zhang schemes. Also the mechanisms by Otomo et al. [52], Shrestha et al. [119] and Stagni et al. [125] were considered, but results are not reported since they predict very low reactivity within the considered temperature range.

At low-intermediate temperatures, H_2 experimental trend with T_{in} is predicted by Nakamura model but values are too overestimated (Figure 11b). At higher temperatures, Song, Glarborg and Zhang mechanisms are able to reproduce H_2 concentration.

Similarly, Nakamura scheme predicts the experimental NO at low temperatures and Song mechanism reproduces the experimental trend at higher ones (Figure 11c).

None of the considered models is able to fully predict the experimental data, and none provides the existence of the three different kinetic regimes experimentally observed.

It is worth highlighting that numerical results significantly differ among them, in particular for low-intermediate temperatures, while they are more consistent for the HT.

4.2. Ammonia oxidation: Dynamic behaviors

In the previous section, NH₃ oxidation under diluted conditions has been characterized through the identification of different regimes, Low, Intermediate and High Temperature. These regimes were identified at steady state condition, as a function of the inlet temperature and mixture stoichiometry. The preliminary campaign also disclosed peculiar behaviors, in terms of evolution of the system from the initial condition to the steady state. Indeed, at ϕ =0.8 and 1, at specific T_{in}, the temporal reactor temperature (T_r) profile passed through damped oscillations.

A literature survey [15,67] suggested that, for various fuels, the transition from lowintermediate temperature oxidation to high temperature burning conditions, coupled with heat exchange phenomena, could promote the onset of thermo-kinetic instabilities. They could have detrimental effects on process energy efficiency and pollutant emissions. For instance, these phenomena in gas turbine applications may also boost the onset of thermoacoustic instabilities and possible mechanical damages. For these reasons, the establishment of dynamic behaviors has been extensively studied for hydrogen and hydrocarbons [15,67]. The JSFRs have been widely used in the scientific literature to identify combustion regimes, bi/multi-stability features with the possibility to stabilize dynamic phenomenologies in virtue of the "continuous flowing" condition and explore the dependence on all the controlling parameters.

Such consideration along with the preliminary results, suggest that dynamic behaviors cannot be ruled out a priori in the transition from the low to the high temperature regime during ammonia oxidation processes. In addition, it is crucial to understand the chemistry and the kinetics involved in this transition, along with its dependence on temperature and mixture composition, to guarantee the stabilization of the high temperature-stable regime, through the implementation of mixing or hot-gas recirculation strategies.

Therefore, further experimental tests were carried out for NH₃/O₂ mixtures diluted in N₂ as a function of mixture stoichiometry and inlet temperatures, at p=1.2 atm and τ =0.21s. The temperature profiles were acquired in time, with high time resolution, in order to detect dynamic phenomena.

A first set of experiments was performed for $NH_3/O_2/N_2$ changing the mixture equivalence ratios ϕ , for fixed T_{in} .

A second set of experiments was performed substituting part of N_2 with H_2O while keeping constant the overall mixtures dilution degree. As it will be explained in the next section, water was used in the attempt of extending the chemical characteristic times in the transition from the low to the high temperature regime. In case of mixture partially diluted in H_2O , further tests were run to investigate the effect of the residence time and dilution level on the oxidation regimes.

The experimental operating conditions are summarized in Table 5.

Conditions	Symbols	Range
Inlet temperature	Tin	1250-1310 K
Equivalence ratio	φ	0.4-1.6
Residence time	τ	0.21, 0.3, 0.5 s
Pressure	Р	1.2 atm
Dilution level	d	80, 82, 84, 86, 88% N ₂
Water content	H ₂ O%	0, 3, 6, 10, 12, 15%

Table 5. Operative conditions explored for the experimental tests for NH₃/O₂/N₂ oxidation.

The first experimental results here reported are relative to inlet temperatures (T_{in}) equal to 1260K, 1280K and 1300K, for ϕ =0.6, 0.8 and 1. Figure 12 reports the characteristic temporal reactor temperature (T_r) for the selected cases, as they univocally define all the combustion behaviors experimentally identified.

Here, it has to be specified that the temporal profiles are reported in a temporal scale up to 100s, in order to clearly show the system behavior case by case. For some profiles, reaching the steady state (STST) takes a longer time with respect to the considered temporal scale. This condition is indicated as "to STST". The extension of the time scale up to the STST for all the conditions would have compromised the readability of the diagram. However, information on the STST for these cases are reported in Figure 13.



Figure 12. Characteristic temporal temperature (T_r) profiles at different ϕ and T_{in} .

At $T_{in}=1260$ K, for $\phi=0.6$, as the fuel is injected (initial time t₀), the reactor temperature slowly increases with the time (t) and after about 50s reaches the stationary steady value (T_r=1285K). This trend is identified as the Low Temperature (LT) regime, characterized by a low reactant conversion (approximately lower than 30%) and a steady state temperature lower than 1300K. This conversion was indirectly derived from the oxygen consumption, because ammonia concentration was greater than the instrument full-scale, thus not quantifiable.

For $\phi=1$, T_r slowly increases, then, when the systems reaches 1300K, the slope of the temporal profile diminishes, suggesting that the reactivity of the system is slightly

decreasing. For $T_r>1310K$, a new change of the curve slope identifies the increase of the system reactivity. This peculiar trend is identified in the manuscript as the Lower Reactivity ("LR").

For ϕ =0.8, the system reactivity is slightly higher than the one reported for the stoichiometric condition. The reactor temperature first increases with a relatively high slope, then, similarly to the previous case, the "LR" regime is identified. It establishes when the system temperature approaches 1300K. In addition, when T_r is approximately equal to 1310K, a dynamic behavior (dashed line), classifiable as damped temperature oscillations in time, is detected. This Dynamic Regime (DR) is identified for 1310K<T_r<1320K. A typical temperature profiles for these instabilities is reported for the next analyzed T_{in} and it will be considered as a reference case for the next analyses. Afterwards, the system temperature increases towards the stationary steady state (not reached within 100s for this case).

For T_{in} =1280K, in general the overall system reactivity increases. In particular, for T_{in} =1280K and ϕ =0.6, the temperature increases monotonically with t, and reaches the final value (T_r =1320K) after about 100s. Differently from the LT regime, this behavior is characterized by a stationary T_r (>1300K) and a full reactant conversion. Therefore, this condition defines the High Temperature (HT) regime.

For the stoichiometric condition, the temperature starts increasing, then, at about 1300K the LR regime establishes and strongly delays the characteristic reactive times. For $T_r>1320K$, the system reactivity increases again. For $\phi=0.8$, the LR regimes is still identifiable, but the transition towards the steady state condition occurs through a dynamic behavior, once again recognized for $1310K < T_r < 1320K$ (dashed line). The inset of Figure 12 magnifies the characteristic temporal profile recorded in this temperature range. It shows a damped oscillation profile as the oscillation amplitude decreases with t. At the same time, the oscillations frequency increases (in the range 1 to 3 Hz), then the system reaches a stationary condition and T_r increases towards the system steady state.

For the last inlet temperature considered (T_{in} =1300K), the overall system reactivity still increases with respect to the other T_{in} . For all the cases, T_r increases monotonically and quickly towards the STST, in agreement with the HT behavior.

It has to be mentioned that the definition of these regimes is congruent with the ones identified in the previous Paragraph 4.1, with the specification that herein the regimes were defined with respect to the reactor temperature (T_r) , to follow the transition among oxidation regimes. In addition, for simplicity, the LT regime here defined includes both the low- and the intermediate- regimes previously described.

Figure 13 provides a full description of the positioning of the combustion regimes with respect to the reactor temperature T_r (at the steady state condition), for T_{in} in the range 1250K-1300K and for ϕ in the range 0.4-1.6.

The conditions where the transition from the LT to the HT occurs through the LR regimes are reported with square symbols. Within the LR regime, the transition through instabilities is indicated by dashed-dotted lines. In addition, in the plane T_r - ϕ , these conditions are highlighted also by a grey area. To better define the ϕ range where dynamic

behaviors were detected within this area, tests were carried out with a step of ϕ equal to 0.2.

In general, as expected, T_r increases with ϕ up to the stoichiometric value ($\phi = 1$), then it decreases.

For T_{in} =1250K, ammonia oxidation occurs through the LT regimes for all the considered mixtures, with a maximum temperature increment of 25K at the stoichiometric condition. For T_{in} =1260K and ϕ <0.6, the temperature increase is moderate (about 25K). These conditions belong to the LT regime. Then, for ϕ =0.7, it increases of about 60K. Afterward, T_r increases with ϕ , peaking at ϕ =1 (T_r =1335K), then it decreases again, and for ϕ =1.6 it is about 1315K.

For $\phi > 0.7$, the HT regime is identified. In particular, for $0.7 < \phi < 1$, the LR behavior is identified (square symbols). For $0.7 < \phi < 0.9$, temperature damped oscillations occur (dotted-dashed lines).

For $T_{in}=1270K$, the LT regime is identified for $\phi < 0.5$. Afterward, for $0.5 \le \phi \le 1$ the system passes from the LT to the HT regime through the LR and damped temperature oscillations (square symbols, dotted-dashed lines, respectively). Instabilities occur for $0.5 \le \phi \le 0.9$. For fuel-rich conditions, the HT regime establishes.

For $T_{in}=1280$ K, the LT behavior is not identified. The reactor temperature is 1325 K for $\phi < 0.4$, peaks at $\phi = 1$ ($T_r=1360$ K), then it decreases with ϕ , reaching 1335 K for $\phi = 1.6$. The temporal temperature profiles have the characteristics attributed to the HT regime. The LR regime is detected in the range for $0.7 < \phi < 1$ (square symbols, dotted-dashed lines) and damped temperature oscillations (dotted-dashed times) occur for $0.7 < \phi < 0.9$.



Figure 13. Reactor temperature T_r as a function of ϕ .

For $T_{in}=1290$ K, the behavior of the system is similar to the one just described, while instabilities and the LR regime establish just in small neighborhood of $\phi=0.8$.

For T_{in} =1300K, all the temperature profiles belongs to the HT regimes. No LR or dynamic behaviors were detected.

To sum up, several combustion regimes were identified and were redefined as follow:

- "Low Temperature" (LT), when Tr does not exceeds 1300K. It is characterized by low ammonia conversion and low temperature increment.
- "High Temperature" (HT), when T_r exceeds the threshold temperature (T_r=1300K), reaching temperature higher than 1320K and higher reactants conversion.
- The transition between these regimes can occur with a monotonic trend or through a "Lower Reactivity" (LR) regime. It is characterized by a decrease of system reactivity in time, detected for T_r between 1300K and 1310K and fuel-lean conditions.
- The LR regime can be followed by a Dynamic Regime (DR), namely temperature oscillations in time, for ϕ in the range 0.5-1 and T_r between 1310K and 1320K.

Figure 14 shows typical oscillations profiles in time for different ϕ at T_{in}=1280K. For these profiles, the initial time is reset to zero just before the onset of the instabilities and the temperature scale is in the range 1300K-1340K to allow the comparison among these profiles.

For all these ϕ values, oscillations start for T_r=1310K and end when T_r approaches 1320K. There are not remarkable differences with respect to the amplitudes of the oscillations (between 1310K and 1340K), while increasing ϕ , the oscillations persist for a shorter time and the frequencies slightly increases. The characteristic frequencies are in the range 1-5Hz.



Figure 14. Temporal temperature profiles for ϕ =0.72, 0.74, 0.76, 0.78, 0.80 and 0.82 at T_{in} =1280K.

The effect of T_{in} on the identified combustion regimes was further investigated considering ϕ =0.8 as the reference case, while changing T_{in} from 1240K to 1310K with a step of 10K (Figure 15).



Figure 15. Temporal temperature profiles for $\phi=0.8$ at different T_{in} (1240K-1310K).

For T_{in}=1240K and 1250K, the temporal temperature profile suggests the establishment of the LT regime. For T_{in}=1260K up to 1290K, the LR behavior occurs when T_r reaches 1300K, followed by temperature approximately oscillations for 1310K<Tr<1320K. Afterwards, the system reaches a stationary condition and Tr increases towards the STST. It is worth noting that the onset of the LR regime slightly depends on the T_{in}, while temperature oscillations occur in a fixed T_r independently from T_{in}. In addition, the LR (along with the dynamic behavior) persists for a shorter time as T_{in} increases. In general, the step through the LR decreases the overall system reactivity and delays in time the achievement of the steady state.

Further experimental tests were performed by replacing N_2 with different amounts of H₂O, keeping constant the mixture overall dilution level. In particular, water concentration was set equal to 3, 6, 10, 12, 15% by volume. As suggested by literature [15,126,127], water was used to slow down the reactivity of the process as an attempt to extend the time interval where dynamic behaviors occur and try to stabilize oscillations as a stationary condition, thus attaining temperature periodic oscillations in time.

Despite the addition of water was not a successful strategy to achieve this condition for the explored conditions, water was able to reduce the overall system reactivity and elongate the time damped oscillation persist. To show at a glance but clearly water effect on the instabilities, the case ϕ =0.8 and T_{in}=1280K was considered as the reference case because instabilities persist for a relative short time. Figure 16a shows the temporal temperature profiles for the above-mentioned water content. In particular, also the temperature oscillations in time are reported in Figure 16b. For these cases, the time scale was reset to 0, relatively to the time they occur in the main figure.

The overall system behavior does not change in presence of water for all the explored conditions, while the system reactivity slows down. For all the water content, T_r passes through the LR behavior with the establishment of damped temperature oscillations in time (T_r =1310-1320K). The onset of instabilities occurs for longer elapsed times and persist for longer times as water content increases. For the mixture diluted in N₂, they persist for 5s, while reaching almost 20s for a water content equal to 15%. When the systems are close to their stationary conditions, the frequency increases to a maximum of 5Hz (for 15% of H₂O).



Figure 16. Temporal temperature profiles for ϕ =0.8 at T_{in} =1280K. $H_2O\%$ =0 (dilution in N_2), 3, 6, 10, 12, 15%.

In any cases, as previously highlighted, the temperature window where damped oscillations are detected is an invariant of the system, since it occurs between T_r =1310-1320K, independently of the water content.

For higher T_r , as the system switches to the HT regime ($T_r > 1320$ K), the temperature profiles intersect at a noticeable T_r (about 1340K), and then water enhances the mixtures reactivity, since T_r is higher than the reference case proportionally to water content.

Because of water elongates the temporal range where dynamic behaviors were detected, further tests were replicated to evaluate the effects of the overall dilution level of the mixtures and the averaged residence times, considering the system $NH_3/O_2/N_2-H_2O(10\%)$ as the reference system.

In particular, Figure 17 reports the experimental temperature profiles obtained for a mixtures with ϕ =0.8 and T_{in}=1280K, while parametrically varying the overall mixture dilution level (*d*) from 80% to 88%, with a step of 2%.



Figure 17. Temporal temperature profiles for $\phi=0.8$ at $T_{in}=1280K$ for the mixture $NH_3/O_2/N_2-H_2O(10\%)$, varying the mixture overall dilution level from 80% to 88%.

For d=88%, the system behavior falls in the LT regime, with a low increment of temperature. The system temperature at the steady state is around 1300K. As the dilution level is decreased to 86%, the system passes through the LR regimes and at 1310K instabilities occur. For all the other cases, the temporal temperature profiles is similar, with the establishment of temperature oscillations in the range 1310K<Tr<1320K. Afterwards all the systems reach the steady state, coherently with the mixture overall dilution level. The transition time through the LR/instability regimes decreases as *d* is decreased.

The final experimental analysis was devoted to evaluate the effect of the residence time (τ) on the ammonia oxidation regimes. Figure 18 reports the experimental temperature profiles obtained for the mixture NH₃/O₂/N₂-H₂O(10%) with ϕ =0.8 and T_{in}=1280K, varying τ (0.21s, 0.35s and 0.5s).



Figure 18. Temporal temperature profiles for $\phi=0.8$ at $T_{in}=1280K$ for the mixture $NH_3/O_2/N_2-H_2O(10\%)$, setting $\tau=0.21s$, 0.35s, 0.5s.

For τ =0.5s, the LT regime can be recognized. The system temperature increased monotonically to its steady state, that does not exceed 1300K. For τ =0.35s and τ =0.21s, the LR regime, along with damped temperature oscillations in time (dashed line) can be identified.

These further analyses show that the dynamic behavior remains confined between $1310K < T_r < 1320K$, independently on the variation of the system parameters, thus confirming this behavior remains an invariant for the ammonia oxidation chemistry. In addition, it is possible to note that the LR regime occurs approximately at around 1300K, with small variations with respect to the operating conditions.

The experimental results were simulated with the aim to identify the positioning of the combustion regimes with respect to ϕ . NH₃/O₂ mixtures diluted at 86% in N₂ and preheated at T_{in}=1280 K at τ =0.21s were analyzed. Results are reported in Figure 19. Temperature oscillations are identified with two dotted lines that, respectively, identify the maximum and minimum temperatures during an oscillation period.

In general, all the mechanisms well reproduce the experimental temperature for $\phi \ge 1.1$, while discrepancies occur for fuel-lean conditions.

Song, Glarborg, Nakamura, Zhang and Konnov mechanisms suggested the occurrence of stationary periodic oscillations for stoichiometric/fuel-lean conditions. As an exemplificative case, a typical temporal profile (obtained by the Nakamura mechanism) is reported in the figure inset. In contrast, Glarborg mechanism predicts stationary steady states for all the considered conditions.



Figure 19. Experimental and numerical temperature profiles as a function of ϕ .

In particular, the Song mechanism predicts temperature oscillations starting from ϕ =0.4 up to ϕ =1. At ϕ =0.4, the amplitude is about 40K, then it increases up to 120K for ϕ =0.6, then it decreases towards the stoichiometric condition. For this mechanism the frequency does not change with ϕ , and it is approximately 5Hz. Afterwards, a steady stationary condition is reached.

Similarly, Zhang mechanism predicts the occurrence of dynamic regimes for $0.4 \le \phi < 1$. A steady stationary state is reached for the stoichiometric and fuel-rich conditions. The oscillations amplitude is 40K for $\phi=0.4$, then it slightly increases with ϕ up to a relative maximum at $\phi=0.5$ (65K), then it decreases to 25K for $\phi=0.7$. Afterwards, it increases again to 120K for $\phi=0.9$. The frequency slightly changes with ϕ . It is 5Hz for $\phi=0.4$, than it increases up to 13Hz for $\phi=0.8$, then it decreases.

Nakamura model predicts temperature oscillations for ϕ between 0.7 and 1.1, with a monotonic increase of the amplitude (from 5 to 95K), while the frequency decreases from 37Hz to 10Hz.

The Konnov one for $0.8 < \phi < 1.1$. The oscillations amplitude is 60K at $\phi = 1$, and it decreases towards fuel-lean conditions (25K for $\phi = 0.8$). Contemporaneously, the frequency increases from 15Hz to 32Hz.

The selected kinetic schemes were further tested against experimental O₂, H₂ and NO profiles for the same reference conditions ($T_{in}=1280K$, d=86%, $\tau=0.21s$) (Figure 20). In the case of temperature oscillations, the numerical concentration are averaged in time with respect to oscillations periods.



Figure 20. Experimental and numerical species concentration profiles as a function of ϕ at T_{in} =1280K, τ =0.21s and d=86% in N₂.

The experimental O₂ profile (Figure 20a) decreases with ϕ to a minimum value at ϕ =1.0, while for higher ϕ it slightly increases again. In agreement with the numerical temperature profiles, Zhang, Nakamura, Song and Konnov kinetic mechanisms are able to predict the experimental O₂ concentration outside the dynamic regimes. Glarborg mechanism well reproduces the experimental O₂ profile for the considered conditions.

NH₃ experimental profile (Figure 20b) is reported for $0.6 \le \phi \le 1$, since outside this range the detected value exceeds the upper range limit of the gas analyzer. Within the considered ϕ range, NH₃ concentration decreases to a minimum value at $\phi=0.9$, then it increases again up to $\phi=1$. For $\phi\le 1$, Konnov, Glarborg and Nakamura mechanisms are able to reproduce NH₃ concentration, while Zhang and Song models predict oscillations for fuel-lean conditions.

H₂ experimental concentration (Figure 20c) is equal to zero for $\phi \le 0.8$, then it increases up to 0.7% at $\phi = 1.2$ and remains constant as ϕ increases. The experimental trend is reproduced by the kinetic mechanisms outside the dynamic regimes but, in general, the numerical profiles overestimate H₂ concentration for fuel-rich conditions. Only the Zhang model is able to reproduce the experimental values with a good agreement.

NO concentration (Figure 20d) is equal to 100 ppm for $\phi=0.4$, then it increases up to 145ppm at $\phi=0.8$. Afterwards, it abruptly decreases for $\phi\geq1$ to a minimum value equal to 30ppm for $\phi=1.6$. For the explored operating conditions, no NO₂ emissions were detected. The experimental NO trend is well reproduced by Glarborg mechanism for $\phi>0.9$, with slightly underestimated values at high ϕ . Also Zhang mechanism predicts the NO concentration for $\phi>1$. Song model overestimates NO concentration for all the explored

conditions. Nakamura and Konnov mechanisms can reproduce the NO experimental data for fuel-rich conditions ($\phi \ge 1.2$).

To sum up, the considered kinetic mechanisms provide better predictions for fuel-rich conditions, under steady state conditions, for both the temperature and species profiles. Although the typology of oscillations (periodic) and the ϕ range where oscillations were numerically predicted are different with respect to the experimental evidences (damped oscillations), models are able to predict a change of oxidation regimes with ϕ .

Once more, these results highlight that models agree on the prediction of the HT regime, while the identification of the LT is very different mechanism by mechanism, with direct consequences on the inconsistent prediction of the DR.

4.3. Kinetic analyses: the inconsistency in the LT oxidation chemistry

The numerical results reported in the previous paragraphs revealed that the considered kinetic mechanisms provide inconsistent results for the prediction of the LT ammonia oxidation, whilst the agreement with the experimental data is more satisfactorily under HT conditions.

In order to understand the sources of such discrepancies, detailed kinetic analyses through flux diagrams, reaction rates and sensitivity analyses were carried out for all the mechanisms.

From an a posteriori analysis, it can be stated that the models provide similar kinetic diagrams for the high temperatures, whereas the low temperature reactivity is described in different ways mechanism by mechanism. Indeed, depending on the mechanism, the LT reactivity can be controlled by the formation of species with higher molecular weight N_2H_x (recombination pathways) or oxygenated species H_xNO (oxidative pathway). Therefore, two mechanisms, specifically Nakamura and Zhang models, were selected to illustrate the main results, because they are emblematic of the recombination and oxidative pathways, respectively.

First, to introduce the main NH_3 oxidation pathways, flux diagrams are herein reported for the stoichiometric condition, at atmospheric pressure and fixed residence time (τ =0.21 s).

Subsequently, the dependence of the oxidation pathways on the mixture equivalence ratio, as well as the mechanisms that determine the onset of instabilities, are discussed through reaction rates and sensitivity analyses.

Each flux diagram reports the main ammonia oxidation reactions, the branching mechanism and the NO formation reactions. In the diagrams, the order of magnitude of all the reaction rates is defined by the color code reported in the legend. Numbers in round brackets represent the multiplying factor to obtain the reaction rate, reaction by reaction. Arrows thickness is proportional to the reaction rate values. The flux diagrams were delineated at fixed temperatures, which are representative of the different oxidation regimes. For the HT regime, the reference temperature for the kinetic studies was fixed

at T_{in}=1350K. For the LT regime, since all the mechanisms behave differently, the reference temperature was chosen at ΔT =10K.

The results according to Nakamura mechanism are reported in Figure 21 (LT and HT). Analyses suggest that NH₃ is converted to NH₂ radicals by reacting mainly with OH for both the considered temperatures, and secondarily with O radicals at low-intermediate temperatures. For the LT, NH₂ mainly recombines to produce diazene (N₂H₂) or hydrazine (N₂H₄) according to the following reactions: NH₂+NH₂=N₂H₂+H₂, NH₂+NH₂+M=N₂H₄+M respectively. Hydrazine dehydrogenation reactions (N₂H₄→N₂H₃→N₂H₂) lead to the formation of N₂H₂ and H₂O₂.

Diazene reacts mainly with HO₂ and secondarily with N₂H₂, H, NH₂ or HNO to produce NNH or N₂H₃. NNH thermally decomposes in N₂ and H. The radical branching mechanism passes through the formation and decomposition of H₂O₂, according to the following reactions: $H+O_2+M=HO_2+M$, N₂H₄+HO₂=N₂H₃+H₂O₂ and H₂O₂+M=OH+OH+M.

NO is formed by HNO according to the reaction $HNO+N_2H_2=NO+N_2H_3$. HNO is produced, in turn, by the reaction between NH_2 and HO_2 . The conversion of NH_2 trough the formation of oxygenated intermediate is considerably slower than the recombination channel. The reactions sequence $NH_2+HO_2=H_2NO+OH$, $H_2NO+NH_2=HNO+NH_3$ and $HNO+O_2=NO=HO_2$ is responsible for the NO formation for the LT regime, nevertheless it is not the controlling reaction pathway.

At $T_{in}=1350$ K, the reaction between NH₂ and H/OH radicals (NH₂+H=NH+H₂ and NH₂+OH=NH+H₂O) overcomes the NH₂ recombination (NH₂+NH₂=N₂H₂+H₂). Additionally, NH₂ oxidation by O radical (NH₂+O=HNO+H) becomes faster. The oxidation pathway NH₂ \rightarrow NH(\rightarrow N₂H₂) implicates the conspicuous H₂ production which produces H radical through H₂+OH=H+H₂O to support the high-temperature branching mechanism (H+O₂=OH+O). Also the reaction H₂O+O=OH+OH plays a key role in OH release.

NO is formed by HNO reactions with H or OH radicals (HNO+H=NO+H₂ or HNO+OH=NO+H₂O). HNO can be obtained directly from NH₂ (i.e. $NH_2+O=NO+H_2$) or from NH reactions with O₂ and OH (NH+O₂=HNO+O and NH+O=HNO). In addition, thermal-NO_x formation (N+O₂=NO+O and N+OH=NO+H) becomes important at these temperatures.



Figure 21. Flux diagrams for NH₃ oxidation at LT (T_{in} =1000K) and HT (T_{in} =1350K) according to Nakamura mechanism.



Figure 22. Reaction pathways at at LT ($T_{in}=1250K$) and HT ($T_{in}=1350K$) according to Zhang mechanism.

The flux diagrams at T_{in} =1250 K and 1350 K according to Zhang mechanism are reported in Figure 22.

As first reaction step, at low temperatures, NH₃ is dehydrogenated by OH radical to produce NH₂, according to the reaction NH₃+OH=NH₂+H₂O. NH₂ is mainly oxidized by HO₂ to produce H₂NO or, secondly, it reacts with NO to produce NNH, which, in turn, is dehydrogenated to N₂. H₂NO mainly produces HNO according to the reactions: H₂NO+O₂=HNO+HO₂, H₂NO+NH₂=HNO+NH₃, H₂NO+HO₂=HNO+H₂O₂. HNO is responsible of NO formation according to HNO+O₂=NO+HO₂.

At high temperatures, NH₂ is dehydrogenated to NH by OH or H. NH reaction paths lead to the formation of N₂ or NO. In the first case, NH reacts with NH₂ according to the reaction NH+NH₂=N₂H₂+H, then N₂H₂ is dehydrogenated to NNH which, in turn, is thermally decomposed to N₂. NO formation mechanism involves the following reactions: NH+H=N+H₂ followed by N+O₂ \rightarrow NO+O or NH+OH=NO+H₂ followed by HNO+H=NO+H₂ or HNO+M=NO+H+M.

The flux diagrams for the other kinetic schemes (not reported here) suggest that, for the high temperatures, all the considered mechanisms describe the ammonia oxidation chemistry through the same main pathways $(NH_3 \rightarrow NH_2 \rightarrow NH(\rightarrow N_2H_2) \rightarrow N_2$ or $NH_3 \rightarrow NH_2 \rightarrow HNO \rightarrow NO$). As a consequence, they provide similar prediction of the main species profiles, with a good consistency with the experimental data.

For low-intermediate temperatures, the chemical routes are mechanism dependent. In particular, the numerical analysis by Konnov mechanism provides results similar to Nakamura, namely NH₃ oxidation at low temperatures passes through the NH₂ recombination reaction (NH₂+NH₂=N₂H₂+H₂). The recombination channel boosts the H₂ formation, indeed both the mechanisms predict higher H₂ concentration with respect to the experimental data. In addition, the conspicuous H₂ formation promotes the reaction H₂+OH=H+H₂O, thus increasing the H radical concentration to sustain the high-temperature branching mechanism and promote the system reactivity at lower temperatures. When the recombination reactions control the oxidation process, the role of the DeNOx reactions is of secondary importance, therefore the numerical NO concentration is greater than the other mechanisms' predictions.

On the other hand, the Glarborg, Song, Shrestha and Otomo mechanisms, similarly to Zhang scheme, identify the formation of oxygenated intermediate species as fundamental step in the ammonia oxidation, emphasizing the role of the reaction $NH_2+HO_2=H_2NO+OH$. Therefore, for these cases, the NH_3 oxidation pathway at low temperatures is described by the sequence $NH_3 \rightarrow NH_2 \rightarrow H_2NO \rightarrow HNO \rightarrow NO(\rightarrow N_2)$. This pathway promotes the formation of NO, that are converted to N_2 by the DeNOx reactions, $NH_2+NO=NNH+OH$ and $NH_2+NO=N_2+H_2O$. The former also contributes to the OH production, but it is too slow to sustain the system reactivity, indeed the OH formation at low-temperature is strictly correlated to the slow NH_2 conversion pathways. The H_2 formation from recombination reactions is marginal, as well as the H_2 role in the H-radical production at low temperatures.

The inconsistency among numerical results themselves and with experimental data as well as the different description of ammonia oxidation pathways have to be correlated also to validating conditions of the considered mechanisms. For the most, the speciation of NH₃ oxidation processes has been evaluated for higher dilution levels and higher working temperatures. Due to the lower thermal power of highly diluted reactant mixtures (d>99%), the mixture ignition is delayed and occurs for higher temperatures.

For these reasons, the models are not able to predict accurately the low-intermediate oxidation features of ammonia mixtures, with a moderate dilution level.

To support this statement, the same mechanisms were tested against further experimental data, for fuel-lean mixture at ϕ =0.8, diluted in N₂ at 99.5% (τ =0.21s, p=1.2 atm). Such dilution level allowed to measure also the NH₃ concentration as a function of T_{in}, since its concentration was lower than the instrument full-scale. Under these operative conditions, the system can be considered isothermal, as confirmed by the measurement of the temperature increment during the oxidation process.

The main species profiles, along with the mechanisms predictions, are reported in Figure 23. The experimental data show system reactivity is slightly delayed by the increased dilution level. Indeed, the NH₃ and O₂ concentrations start to decrease for T_{in} >1225K, albeit their profiles exhibit a lower slope with respect to the previous results, therefore the complete conversion is achieved for T_{in} >1330K. The H₂ concentration varies from 250ppm at T_{in} =1200K up to a maximum of 300 ppm at T_{in} =1260K, then it decreases to 50 ppm at 1350K. For the considered temperature range, the NO profile has a monotonic increasing trend from 50ppm up to 270ppm at 1350K.

The numerical predictions are more consistent with the data for such operative conditions. In particular, the Shrestha and Zhang models reproduce perfectly the NH₃ and O₂ profiles, whereas the other schemes predict a slightly higher reactivity. The H₂ profile is well predicted by Konnov mechanism for T_{in} >1250K. Nakamura model reproduces the H₂ trend, with higher concentrations. The other schemes can predict the experimental trend, underestimating the concentrations. The NO profile is predicted by Nakamura, Zhang and Shrestha mechanisms for T_{in} =1200-1300K. For higher T_{in} , the mechanisms by Glarborg and Konnov provide better results.



Figure 23. Experimental (symbols) and numerical (lines) NH₃, O_2 , H_2 and NO profiles for a lean (ϕ =0.8) NH₃/ O_2 mixture diluted in N₂ at 99.5%, at atmospheric pressure and τ =0.21s.

The kinetic analyses carried out for such operative conditions revealed more consistent reaction pathways for NH₃ oxidation. Even though the recombination pathway trough the reaction $NH_2+NH_2=N_2H_2+H_2$ plays a more important role for Nakamura and Konnov mechanisms, as perceivable from the higher numerical H₂ concentration, it is balanced by the formation of HNO and the DeNO_x reactions.

Indeed, since the system reactivity is shifted towards higher temperatures due to the high dilution level, the HT chemistry controls the oxidation process, therefore the kinetic analyses showed more coherent results.

These findings support the previous discussion and confirm the necessity to improve the mechanisms performance for the low-intermediate oxidation regime, relevant for the prediction of the mixture oxidation under MILD operating conditions.

4.4. Kinetic analyses: the role of NH₂ radicals in NH₃ dynamic regimes

The previous kinetic analyses assessed the relevant role of the NH₂ paths in NH₃ oxidation for both the LT and the HT regimes. Despite the different interpretation of the LT chemistry, an effort to understand the controlling kinetics for the onset of the dynamic regimes was numerically realized by Reaction Rates analyses.

The numerical analysis was carried out as follow. Since the onset of dynamic behaviors depends on ϕ and T_{in}, the main oxidation pathways at steady conditions were identified

through flux diagrams at low and high temperatures for fuel-lean and fuel-rich conditions (ϕ =0.4, ϕ =1.2) and, then, the relative reaction rates (RRs) analyses for 900K<T_{in}<1400K are reported. This methodology allows the identification of the main controlling pathways at different equivalence ratios outside the instabilities range. As a final step, particular attention is dedicated to the characterization of the reaction pathways at ϕ =0.8, where oscillations were experimentally and numerically detected.

Firstly, the discussion is lead based on Nakamura mechanism, then the results obtained by Zhang model are presented.

The preliminary study through the flux diagrams (not reported here) revealed that the low-temperature reactivity does not change drastically with ϕ , since NH₃ oxidation occurs through the same reactions identified in Figure 21. The overall NH₃ reaction pathway at LT can be summarized as follows: NH₃ \rightarrow NH₂ (\rightarrow N₂H₄ \rightarrow N₂H₃) \rightarrow N₂H₂ \rightarrow NNH \rightarrow N₂. The OH production depends on N₂H_x chemistry through H₂O₂ formation and thermal decomposition. To some extent, this result is consistent with the experimental evidences, that suggest the LT regime is not strongly affected by the mixture stoichiometry.

On the contrary, the high-temperature oxidation chemistry depends more significantly on the ϕ .

At fuel-lean condition, NH₂ radicals, mainly produced via NH₃+OH=NH₂+H₂O, can recombine to N₂H₂ (NH₂+NH₂=N₂H₂+H₂) or react with OH radicals, according to the reaction NH₂+OH=NH+H₂O. As for low temperatures, N₂H₂ is subsequently dehydrogenated to N₂, following the reactions N₂H₂+HO₂=NNH+H₂O₂ and NNH+M=N₂+H+M. This reaction mainly contributes to the release of H radicals that feed the typical H₂/O₂ high-temperature branching mechanism, namely H+O₂=OH+O and H₂O decomposition (H₂O+O=OH+OH).

NH radicals are responsible of NO formation via the reactions $NH+O_2=HNO+O$ and $HNO+OH=NO+H_2O$. Secondarily, NH can react with NO to produce N_2O (NH+NO=N₂O+H), which decomposes in N₂ and O (N₂O+M=N₂+O+M).

At fuel-rich condition, in presence of a high H concentration, NH₃ can be dehydrogenated to NH₂ by both OH (NH₃+OH=NH₂+H₂O) and H (NH₃+H=NH₂+H₂) radicals. NH₂ is N_2 through the recombination mainly converted to pathway $(NH_3 \rightarrow NH_2 \rightarrow N_2H_2 \rightarrow NNH \rightarrow N_2)$. Secondarily, NH₂ reacts with H radicals to produce NH (NH₂+H=NH+H₂), which decomposes to N and H according to the reaction NH+M=N+H+M. N can react with NH₂ to produce N₂ (N+NH₂=N₂+H₂) or it is responsible of NO formation through the reaction N+O₂=NO+O. It is worth noting that both the recombination $(NH_3 \rightarrow NH_2 \rightarrow N_2H_2 \rightarrow NNH \rightarrow N_2)$ and the dehydrogenation $(NH_3 \rightarrow NH_2 \rightarrow NH \rightarrow N \rightarrow N_2)$ pathways provide significant H₂ production. Therefore, due to the higher H₂ concentration for fuel-rich conditions, the branching mechanism is driven by the high-temperature reactions of the H₂/O₂ system, namely H₂+OH=H+H₂O and H+O₂=OH+O, thus it is not dependent directly on nitrogen species reactions.

The transition from the LT to the HT kinetics as a function of the stoichiometry is more clearly discussed by the RRs analyses. Figure 24 show the rate of the main reactions as a function of T_{in} at $\phi=0.4$ and 1.2.

At ϕ =0.4 ammonia conversion to NH₂ via H-abstraction is the fastest reaction within the whole temperature range and consumes OH radicals, that are provided by the H₂O₂ decomposition for low temperatures (T_{in}<1050K) and by the reaction H+O₂=OH+O for T_{in}>1050K.

NH₂ consumption reactions depends on the temperature. For T_{in}>1300K, NH₂ is mainly oxidized by OH radicals to NH. At temperatures lower than T_{in}<1300K, two NH₂ radicals react to form H₂ and N₂H₂. Subsequently, diazene dehydrogenation pathway provides H₂O₂ by means of the reaction N₂H₂+HO₂=NNH+H₂O₂ and also H radicals through the reaction NNH+M=N₂+H+M. The latter reaction is the main source of H radicals for T_{in}<1120K and T_{in}>1250K. At intermediate temperatures (T_{in}=1120-1250K), due to NH₂ recombination, H₂ concentration increases thus H₂ oxidation (H₂+OH=H+H₂O) becomes as fast as the NNH dehydrogenation and provides H radicals. Nevertheless, as the temperature increases, NH₂ oxidation (NH₂+OH=NH+H₂O) becomes faster than NH₂ recombination and, consequently, H₂ concentration decreases and the rate of the reaction H₂+OH=H+H₂O falls to zero.



Figure 24. RRs analysis for the main reactions of $NH_3/O_2/N_2$ system as a function of T_{in} at $\phi=0.4$ and 1.2, according to Nakamura mechanism.

At ϕ =1.2, NH₃ is oxidized to NH₂ and H₂O by OH radicals for T_{in}<1310K, while it is dehydrogenated to NH₂ and H₂ by H radicals for higher temperatures. As for ϕ =0.4, also under fuel-rich conditions two NH₂ radicals react to produce diazene and hydrogen for T_{in}<1300K. At higher temperatures, NH₂ reacts mainly with H radicals to produce NH and H₂. Both NH₂ reaction pathways contribute to increase H₂ concentration. As a consequence, H₂ oxidation by OH radicals becomes faster and faster as the temperature increases, thus the reaction H₂+OH=H+H₂O is the main source of H radicals for T_{in}>1140K (for lower temperatures H radicals come for the most from NNH decomposition). In addition, H₂ oxidation competes against NH₃ oxidation for OH consumption, thus the latter reaction starts to decrease at T_{in}=1190K and becomes slower than H₂+OH=H+H₂O for T_{in}>1250K. The radicals that sustain the branching mechanism come from H_2O_2 decomposition for $T_{in} < 1100$ K, while at higher temperatures they are provided by the reaction $H+O_2=OH+O$. Once identified the controlling chemistry for ultra-lean and rich mixtures, RR analyses were repeated also for $\phi=0.8$, where experimental and numerical dynamic behaviors were obtained.

In Figure 25 rates of the controlling reactions for the LT and HT regimes at ϕ =0.8 are reported. The grey area represents the temperature range in which oscillations occur.

The NH₃ main kinetic pathways for LT and HT are similar to the ones identified at ϕ =0.4. In particular, the pathway NH₃ \rightarrow NH₂ \rightarrow N₂H₂ \rightarrow NNH \rightarrow N₂+H controls the LT oxidation and the NH₃ high temperature route is mainly represented by NH₃ \rightarrow NH₂ \rightarrow NH \rightarrow N₂ or NH₃ \rightarrow NH₂ \rightarrow NH \rightarrow HNO \rightarrow NO. The low temperature branching mechanism is driven by H₂O₂ decomposition (H₂O₂+M=OH+OH+M). As the system temperature increases, the high temperature H₂/O₂ branching mechanism (H+O₂=OH+O, H₂+OH=H₂O+H) enhances its relative importance, but its leading role is inhibited by the scarce H production. In fact, for T_{in}<1100K the H radical release depends on NNH production limited by the low reaction rates N₂H₂+HO₂=NNH+H₂O₂.

Therefore, the RRs analysis suggests to relate the overall-system reactivity to H radical production. The evidence that the high temperature branching mechanism (initiated by $H+O_2=OH+O$) of the H_2/O_2 sub-system does not cover a relevant role for temperatures much higher than the classical cross-over one [128,129], indirectly denounces the incapability of the slow NH₃ to sustain the radical branching mechanism. Thus, the simplest way to read the ammonia chemistry is to emphasize the H radical production routes within the ammonia oxidation chemistry. As a matter of fact, temperature oscillations occur when H radicals are produced through the reaction $H_2+OH=H_2O+H$, thus relieving the system reactivity from the ammonia slow oxidation pathways. In Figure 25 such a condition is represented by the empty circle at $T_{in}=1100K$. The system comes out the oscillatory behavior when the reaction rate of NH₂+OH=NH+H₂O overcomes the NH₂+NH₂=N₂H₂+H₂ one (empty square at $T_{in}=1290K$). In fact, the reactions of the NH radical, along with the H₂ oxidation, releave the H production from the NNH decomposition and promote the high-temperature branching mechanism.

To sum up, the LT regime is determined by the low temperature H₂ branching mechanism coupled with NH₃ slow chemistry to H radical production. As T_{in} increases, the system reactivity is fastened by the increasing importance of the H₂ high temperature branching mechanism, that is not supported by the slow ammonia chemistry, thus dynamic phenomenology establishes. As T_{in} increases, the ammonia oxidation pathways pass through a faster direct oxidation of amino radicals that can sustain the H₂ high temperature branching mechanism, thus the system achieves a steady stationary state.



Figure 25. RRs analysis for the main reactions of $NH_3/O_2/N_2$ system as a function of T_{in} at $\phi=0.8$, according to Nakamura mechanism.

Simultaneously, the same analyses were replicated for Zhang mechanism. Similar conclusions were achieved concerning the effect of the mixture stoichiometry on the oxidation pathways, namely it does not affect the LT reactivity, while the HT chemistry exhibits a stronger dependence on ϕ . Therefore, the main results are herein reported at ϕ =0.9, where oscillations were detected.

From Figure 26, for $T_{in}<1270$ K, it is inferred that the NH₂ is converted by the reactions NH₂+HO₂=H₂NO+OH and NH₂+NO=NNH+OH and NH₂+NO=N₂+H₂O. Even though the DeNO_x reaction NH₂+NO=NNH+OH may provide directly OH radical to sustain the oxidation process, it is conditioned by the slow NO formation though the following pathway: NH₂ \rightarrow H₂NO \rightarrow HNO \rightarrow NO. Therefore, the OH production depends on the reactions NH₂+HO₂=H₂NO+OH and H+O₂=OH+O and H radicals come from NNH decomposition.

For $T_{in}>1310K$, outside the oscillations region, the reaction $NH_2+OH=NH+H_2O$ controls the oxidation process and both $NH_2+NH=N_2H_2+H$ and $NH_2+H=NH+H_2$ contribute to increase the system reactivity, while the role of $NH_2+HO_2=H_2NO+OH$ becomes marginal. The branching mechanism $H+O_2=OH+O$ is sustained by the H production through both $NNH=N_2+H$ and $H_2+OH=H+H_2O$.

The transition from the LT to the HT ($T_{in}=1270-1310K$) is characterized by a competition between the LT oxidation pathway ($NH_2 \rightarrow H_2NO \rightarrow HNO$) and the HT one ($NH_2 \rightarrow NH \rightarrow N_2H_2$), thus determining the onset of instabilities.

Apart of the detailed pathways case by case, passing from the LT to the HT the numerical simulations suggest a delicate balance between the reactions of NH₃ and H₂. The nub of the ammonia oxidation chemistry is the relative importance of NH₃ and H₂ direct reactions with OH radicals (reactions NH₃+OH=NH₂+H₂O and H₂+OH=H₂O+H). This competition is emphasized by a slave relationship of H₂ production from NH₂ recombination and/or dehydrogenation pathways.



Figure 26. RRs analysis for the main reactions of $NH_3/O_2/N_2$ system as a function of T_{in} at $\phi=0.9$, according to Zhang mechanism.

In particular, for fuel ultra-lean conditions, the mixture stoichiometry limits the system reactivity by a poor release of H radicals (necessary to sustain the H₂ high temperature branching reaction), limiting both H₂ production, thus the reaction $H_2+OH=H_2O+H$, and the NNH formation and decomposition. Increasing the system temperature, the conversion of NH₂radicals to NH relieves the system dependence from the H₂ production. For the conditions where instabilities are detected, the mixture stoichiometry allows for a conspicuous H_2 production that can sustain the H_2 high temperature branching reaction. During and oscillation period, the reaction rate of $H_2+OH=H_2O+H$ is faster than NH₃+OH=NH₂+H₂O one. The competition for OH radicals determines the onset of temperature oscillations, as the H₂ oxidation limits the H₂ production itself, because it consumes OH radicals necessary to produce H₂ from NH₂. The system comes out instabilities when the role of H₂ as source of H radicals is not fundamental, as NH₂ is mainly converted to NH, and then H radicals, thus fastening the overall system reactivity. For fuel-rich conditions, the leading role of H_2 as source of H radicals is not competitive with NH₃ oxidation for OH radicals, because NH₃ is mainly dehydrogenated by H radicals to H₂radicals. H₂oxidation is just limited by the scarce O₂ concentration. In addition, H₂ production is sustained not only by NH2 recombination to N2H2, but also by NH2 dehydrogenation to NH (NH₂+H=NH+H₂). For the HT, the H radicals to sustain the H_2 high temperature branching mechanism come from the NH radicals.

Therefore, the most important aspects, inferable from the overall analysis of NH₃ chemistry, are listed below:

1. Analyzing the system behavior as a function of ϕ , for ultra-lean conditions the oxidation process is leaded by NH₃ reactions. For fuel-rich conditions, the H₂ direct oxidation controls the overall system reactivity. For the conditions where instabilities are predicted, the competition between NH₃ and H₂ direct oxidation, with a master-slave relationship, determines the onset of oscillations. The delicate

interplay between these reactions is considerably dependent on the mixture stoichiometry, since as ϕ increases toward the stoichiometric conditions, the role of H₂ is emphasized and supported by the high O₂ content, then the competition is relaxed. This consideration is supported also by the features of damped oscillations with ϕ (Figure 14). In fact, they persist for a shorter time while increasing ϕ , since the importance of the H₂ direct oxidation chemistry increases. The end of instabilities for fuel-rich conditions has to be related to the direct dehydrogenation of NH₃ to form H₂ by H radicals, given the scarcity of O₂, thus the competition between NH₃ and H₂ ceases.

2. For any mixture composition, the HT regime chemistry has to be correlated to the H₂ high-temperature branching reaction, supported by the direct dehydrogenation of NH₂ to NH radicals (instead of NH₂ recombination). The H radicals, that feed the high temperature branching mechanism, derive from different pathways depending on the mixture stoichiometry.

Despite such overall controlling mechanisms were identified for different kinetic models, it must be stressed that description of the ammonia LT chemistry is mechanismdependent, with direct consequences on the prediction of dynamic regimes and then to the shift from LT to HT regimes.

4.5. Oxidation of NH₃-NO system

The oxidation of NH_3 -NO mixtures has been extensively studied under operating conditions relevant for the thermal-DeNO_x process, namely traces of NH_3 and NO, for lean conditions, in the temperature window 1100-1300K [39]. Experiments were also performed in flow reactors for high temperature and high dilution conditions.

Recently, Alzueta et al. [130] studied the interaction of NH₃ and NO in a quartz tubular flow reactor at atmospheric pressure and temperatures in the range 700-1500K, from fuel lean to fuel rich conditions, evaluating different NH₃/NO ratio. They found that the reduction of NO occurs efficiently at almost any equivalence ratio, with a marginal sensitization effect when varying the NH₃/NO ratio. Based on numerical investigation, they identified the NH₂+NO as controlling reaction mechanisms under any stoichiometry. Dagaut [131] performed experimental and numerical investigation on highly diluted NH₃-NO mixtures in a Jet Stirred Reactor, for several initial concentration of NH₃ and NO, for various equivalent ratios (0.1, 2) at atmospheric pressure and variable temperature (1100-1450K).

Despite these scientific contributions, NO formation/reduction chemistry and the NH₃-NO interaction is not still properly addressed, especially under low temperatures (< 1400K). This has consequence also the description of ammonia oxidation. Indeed, as demonstrated in the previous paragraphs, the reaction pathways controlling the oxidation of pure ammonia mixtures, in particular under low temperatures, are strongly influenced by the formation and reduction mechanisms of nitrogen oxides.

In order to assess the role of NO formation/reduction chemistry in NH₃ oxidation regimes, further experiments were performed for NH₃-NO/O₂ mixtures diluted in N₂ at 86% as a function of the inlet temperature in the range 900-1350K, under nearly atmospheric pressure (1.4 atm), at fixed residence time (τ =0.21s) and equivalence ratio (ϕ =0.8). Experiments were carried out for mixtures doped with 450 and 800 ppm of NO, then the main species profiles were compared with those of the reference case, namely pure NH₃ at ϕ =0.8 (reported in Paragraph 4.1).

The considered operating conditions are summarized in the Table 6.

Conditions	Range
Inlet temperature (T _{in})	900-1350 K
Equivalence ratio (φ)	0.8
Residence time (τ)	τ=0.21s
Pressure	1.4 atm
Dilution level (d)	86% in N ₂
NO initial concentration	450, 800 ppm

Table 6. Experimental operative conditions for NH₃-NO oxidation tests.

Figure 27 shows the concentration profiles of main species (O₂, H₂, NO) detected for pure NH₃ (black symbols) and NH₃-NO oxidation (green symbols NO=450 ppm, red symbols NO=800 ppm).

In general, O₂ concentration starts decreasing for T_{in} =1100K and a significant O₂ conversion occurs for T_{in} >1300K. It can be observed that NO does not alter significantly the system reactivity.



Figure 27. Experimental species profiles as a function of the temperature for NH₃ and NH₃-NO mixtures oxidation, at ϕ =0.8, diluted in N₂ at 86%.

The NO profile (semilogarithmic scale) for the pure NH₃ exhibits the peculiar nonmonotonic trend at low temperatures, as previously discussed. NO concentration increases up to 50ppm at T_{in} =1150K, then it decreases down to a minimum value (30ppm) for T_{in} around 1250 K. Afterwards, it increases again with T_{in} . For T_{in} =1380K, NO is about 160 ppm. For mixtures doped with NO, the concentration of NO remains equal to the initial value for T_{in} <1000K, while an abrupt NO concentration decrease
occurs for T_{in} close to 1100K, independently of NO initial concentration, suggesting the occurrence of fast DeNO_x reactions (NH₂+NO=NNH+OH and NH₂+NO=N₂+H₂O). For T_{in}>1150K, regardless of the initial NO concentration in the mixture, NO profiles almost overlap. At higher temperatures, such reactions are less favored and the occurrence of faster NO formation routes determines the increase in NO concentration.

Pure NH₃ and NO-doped mixtures exhibit the same hydrogen profile, as reported in Figure 27b. H₂ concentration starts increasing for T_{in} around 1000K and peaks at T_{in} =1150K, then it decreases with T_{in} .

Numerical simulations (not reported here) were performed using the detailed kinetic mechanisms by Glarborg, Zhang, Stagni and Shrestha, to evaluate their performance against NH₃-NO experimental data. In general, apart from Shrestha model, the selected mechanisms envisage similar predictions for both NH₃ and NH₃-NO oxidation, namely they are not able to capture the NO trend for the oxidation of pure NH₃ for the low temperatures, while the agreement between experimental and numerical profile improves for higher temperatures. In case of NH₃-NO mixtures, the NO profile is better described, even though the onset of NO reduction is slightly shifted at higher temperatures compared to experiments. As also found in previous paragraphs, the H₂ trend is not reproduced and its formation is underestimated for temperatures lower than 1300K.

4.6. Thermal decomposition of ammonia

According to the kinetic analyses reported in the Paragraph 4.3, the recombination reactions of NH_2 radical to N_2H_x species and their subsequent decomposition to H_2 and N_2 play an important role in ammonia oxidation under low-intermediate temperatures.

Several literature papers agree on the importance of ammonia decomposition reactions for the characterization of NH₃ combustion, in particular under fuel-rich conditions. Despite the importance of such topic, the thermal decomposition of ammonia is not well assessed and few works describe the chemistry behind this process, in general under very high temperatures, thus not relevant for MILD applications .

Not least, understanding the thermal decomposition process of ammonia to hydrogen (and nitrogen) may be relevant to its applications as a hydrogen carrier.

Under pyrolytic conditions, the possible occurrence of interactions with reactor surface cannot be a-priori ruled out, even though it was previously demonstrated that NH₃ oxidation is not affected by heterogeneous reactions, for the operative conditions of interest. Indeed, the thermal decomposition occurs through slower characteristic kinetic times, thus comparable with the heterogeneous ones. Numerous works evaluated the possible impact of the reactor materials on the ammonia decomposition process and show that a surface passivation may mitigate this gas-solid interaction (as reported in the Paragraph 2.1.3.).

Based on these consideration, experimental tests on ammonia pyrolysis were conducted following the procedure discussed in the Paragraph 3.4, in order to keep into account the

effects of the surface interactions on the processes. Therefore, NH₃/Ar (d=92%) and NH₃/Ar-H₂O (d=90.5% Ar, 1.5% H₂O) were analyzed, since water was used to passivate the quartz surface. Furthermore, the analyses proceeded throughout experimental tests in LFRs to value the heterogeneous effects with different materials.

Ar was chosen as bath gas in order to highlight the N_2 formation from NH_3 decomposition. The experimental tests were performed at atmospheric pressure and fixed residence time (0.25s) in the JSFR and fixed velocity (3 m/s) in the LFRs.

The operative conditions are summarized in Table 7.

Conditions	Range
Inlet temperature (T _{in})	900-1350 K
NH ₃ concentration	8%
Residence time (τ) or velocity (v)	τ=0.25 s (JSFR), v=3m/s (LFRs)
Pressure	1.2 atm
Diluent (d)	92% Ar, 90.5% Ar - 1.5% H ₂ O

Table 7. Experimental operative conditions for NH₃ pyrolysis tests.

The main results for the pyrolysis of NH₃/Ar and NH₃/Ar/H₂O mixtures in the JSFR are reported in Figure 28.

For both the mixtures, H_2 and N_2 profiles suggest that the decomposition starts at $T_{in}>1150$ K. In presence of H_2O the amount of H_2 and N_2 result to be lower. The more the temperature increases, the more these differences become important.

These data suggest that heterogeneous reaction affects NH₃ decomposition more than NH₃ oxidation, because of slower or comparable pyrolytic characteristic kinetic time with respect to heterogeneous ones. In the case of ammonia oxidation, such effects are maybe reduced because oxidation characteristic times are shorter than heterogeneous ones.



Figure 28. H_2 and N_2 experimental profiles as a function of T_{in} , for the pyrolysis of NH_3/Ar (d=92%) and $NH_3/Ar/H_2O$ (d=90.3% Ar-1.7% H₂O) mixtures, at fixed p=1.2 atm and τ =0.25 s, in JSFR.

The effectiveness of the water surface passivation was evaluated for two fixed temperatures (T_{in} =1220, 1270 K) by changing the amount of H₂O in initial composition (Figure 29).

Results show that an increase of the H_2O concentration does not further reduce H_2 and N_2 concentration. This may suggest that surfaces could be considered passivated when the H_2O content is set equal to 1.7%. Thus, even if it is not a straightforward proof that steam passivates the surface, such results are comforting, and seem to suggest that at least steam minimizes these heterogeneous effects.

In addition, this behavior is not likely to be ascribable to homogeneous kinetic effects related to the water decomposition, since it would occur in presence of O radicals according to reaction $H_2O+O=OH+OH$ [126,132]. In these operative conditions, no oxygen is fed to the system, thus no O radicals would be present in the gas phase.



Figure 29. H_2 and N_2 concentrations as a function of H_2O content for the pyrolysis of $NH_3/Ar/H_2O$ (overall d=92%) mixtures, at fixed temperatures (T_{in} =1220, 1270 K), p=1.2 atm and τ =0.25 s, in JSFR.

The experimental results in the LFRs facility are reported in Figure 30. For these operative conditions, the detected species profiles exhibit significant differences depending on the material. Coherently with the results obtained in the JSFR, H₂ and N₂ trends suggest that the NH₃ conversion starts at around T_{ref} =1150 K for both the reactors and the decomposition is enhanced increasing the temperature. The higher H₂ and N₂ concentrations found for the alumina reactor, with respect to the fused silica one, highlight the strong impact of surface reactions on the ammonia thermal decomposition. Nonetheless, the onset of ammonia decomposition was found to occur at the same temperature (about 1150K) independently of heterogeneous reactions.

The former results are confirmed by the recent work of Benés et al. [133], that investigated ammonia pyrolysis in both a quartz tubular flow reactor (900–1500 K) and a non-porous alumina tubular flow reactor (900–1800 K) using Ar or N₂ as bath gas, for ammonia inlet concentration in the range 1000-10000 ppm. They found that ammonia pyrolysis at atmospheric pressure begins at 1173 K. Nevertheless, the impact of surface material was not observed for temperatures lower than 1400K.



Figure 30. H_2 and N_2 experimental profiles as a function of T_{ref} , for the pyrolysis of NH_3/Ar (d=92%) mixture at atmospheric pressure and v=3 m/s, in LFRs.

The experimental results were simulated using the different kinetic mechanisms previously described. In this context, it is worth highlighting that the data obtained with the LFRs are not easy to model, because T_{ref} is not indicative of the real thermal state of the reactive mixtures. Thus, the data previously reported give important information relatively to the interaction of ammonia homogeneous/heterogeneous chemistry with different materials, but they cannot be straightforwardly used for modeling activities. For this reason, simulations were performed considering the data from the JSFR.

The comparison between experimental and numerical profiles is shown in Figure 31.



Figure 31. Experimental and numerical H_2 profiles for NH₃ pyrolysis diluted in Ar-H₂O, at fixed p=1.2 atm and $\tau=0.25$ s, in JSFR.

The agreement between experimental and numerical profiles is worse for the pyrolysis process if compared to the numerical predictions of the oxidation process. Indeed, H_2 and N_2 numerical profiles obtained by Glarborg and Song mechanisms are almost zero in the entire investigated temperature range, while Nakamura and Shrestha models show a slight

 NH_3 decomposition for T_{in} =1200-1300K even though the species concentrations are remarkably lower with respect to the experimental values.

These results bring to light the grave inconsistency of the kinetic schemes to describe ammonia thermal decomposition. Indeed, the mechanisms are not satisfactorily tuned to describe ammonia pyrolysis and, perhaps, this aspect could affect also the prediction of the main features of ammonia oxidation.

To corroborate the previous statements, the experimental results reported in the Paragraph 3.4 for the oxidation of NH₃/O₂/Ar mixture are here reconsidered, in order to assess the role of the ammonia pyrolysis in the oxidation process.

In particular, the direct comparison between N_2 profiles (considered as inert species) under oxidative (from Figure 6) and pyrolytic (from Figure 28) conditions, for the mixtures partially diluted in water, shows that they overlap, thus suggesting that ammonia decomposition kinetics may have a relevant role for the LT oxidation (Figure 32).



Figure 32. Comparison between N₂ profiles from ammonia oxidation (NH₃/O₂/Ar/H₂O mixture, d=86%, ϕ =1.0, p=1.2 atm, τ =0.25 s) and ammonia pyrolysis (NH₃/Ar/H₂O mixture, d=92%, p=1.2 atm, τ =0.25 s) in JSFR.

4.7. Kinetic analysis on ammonia pyrolysis

Reaction rate and sensitivity analyses were performed in order to highlight the controlling reactions of NH₃ pyrolysis. Understanding the chemistry under pyrolytic conditions represents a critical issue with strong implication also for the low-intermediate temperatures, as stated by several scientific works. In fact, experimental evidences from several facilities show that the ammonia pyrolysis occurs at temperatures relatively lower with respect to the predicted ones, in agreement with results presented in this thesis.

Monnery et al. [134] performed ammonia pyrolysis tests in a tubular quartz reactor for NH₃/Ar mixtures by changing NH₃ concentration from 0.5 to 2%. They found that at 1123 K ammonia conversion is around 3-4% for a mixture residence time equal to 0.18 s and

5-6% increasing the residence time to 0.4 s. These results are compatible with the ones obtained in the quartz LFR reported in the paragraph 3.4, as at T_{ref} =1120 K and residence time equal to 0.2 s, the measured NH₃ conversion is around 5%.

In addition, Rahinov et al. [90] evaluated the decomposition of ammonia in a quartz tubular reactor. Quartz surface was passivated with ammonia. They found out that NH₂ is formed via gas-phase ammonia decomposition at 950 K, thus indicated the onset of NH₃ pyrolysis reactions.

Kobayashi et al. [66] presented an overview of available kinetic mechanisms of ammonia oxidation and fuel NOx. In particular, they analyzed the work by Miller et al. [120] and highlighted that their kinetic model was able to predict the experimental data for fuel lean flames under low pressure (20-50 Torr), but failed to predict data for stoichiometric and fuel rich conditions. They suggested that the ammonia pyrolysis reaction rates are strongly underestimated in the kinetic mechanism with strict consequences also for ammonia oxidation prediction.

This aspect is even more evident for the prediction of ammonia ignition delay time. Mathieu and Petersen [82] stressed how their model and Klippenstein et al.'s mechanism [114] differ in prediction of ignition delay times due to the different intermediate-sensitivity reactions and, particularly, they remarked the differences in the pyrolysis reactions (that involve NH_2 and N_2H_2 without involvement or molecular or atomic oxygen).

Herein, key species sensitivity analyses were realized at T_{in} =2000 K, where H₂ concentrations were equal for all the mechanisms.

The bar diagrams (Figure 33) show the maximum values of the sensitivity coefficients with respect to the temperature for the main reactions involved in H_2 and N_2 formation, according to the considered models.

The sensitivity analysis suggests that for Song and Glarborg models, H₂ and N₂ exhibit high sensitivity to the same reactions. In particular, the maximum positive sensitivity occurs for reactions: $NH_3(+M)=NH_2+H(+M)$, $NH_2+NH_2=N_2H_2+H_2$, $N_2H_2+M=NNH+H+M$.

This set of reactions is different for the Nakamura scheme. In this case, the maximum positive sensitivity values for H_2 and N_2 occur for reactions:

N₂H₂=NNH+H, N₂H₃=N₂H₂+H, NH₃+NH₂=N₂H₃+H₂.

A similar reactions set was identified as important also for lower temperatures (not reported here) relevant for the conditions explored in this thesis, thus suggesting the generality of these results.



Figure 33. Sensitivity analyses for NH₃ pyrolysis at T_{in} equal to 2000 K.

The main reaction pathways were identified by means of flux diagrams. For the sake of briefness, the results obtained by Song mechanism were not reported, since they are similar to the ones obtained by Glarborg model (as also suggested by the sensitivity analysis). In the flux diagrams (Figure 34), the order of magnitude of all the reaction rates is 1E-1 and values reported in round brackets represent the multiplying factor. Arrows thickness is proportional to the reaction rate values.



Figure 34. Main reaction paths in NH_3 pyrolysis according to Glarborg and Nakamura mechanisms, at T_{in} =2000 K.

Referring to Glarborg model, NH₃ decomposes to NH₂ according to the reactions: NH₃+H=NH₂+H₂ and NH₃+H+M=NH₂+H+M. NH₂ is directly converted to N₂H₂ (NH₂+NH₂=N₂H₂+H₂) or is dehydrogenated to NH (NH₂+H=NH+H) and, subsequently, NH reacts with NH₂ to produce N₂H₂. N₂H₂ mainly isomerizes to H₂NN, which, in turn, decomposes to N₂ and H₂. Alternatively, N₂H₂ is dehydrogenated to NNH, which decomposes to N₂.

The analysis of the flux diagram obtained by Nakamura model suggests similar reaction pathways.

The main difference among the two mechanisms lays in the description of N_2H_2 consumption reactions. In particular, Nakamura model does not involve H_2NN , since N_2H_2 reacts with H to produce NNH and H_2 .

Disregard the differences between the description of ammonia pyrolysis, the agreement with experimental data is not satisfactory. Beyond the occurrence of material catalytic effects, this aspect is well supported by literature evidences. Therefore, the comprehension of this chemistry seems to be prohibitive at the moment. This aspect would require a peculiar attention, also because strictly connected with the ammonia oxidation kinetics.

4.8. Oxidation of ammonia-hydrogen systems

4.8.1. Effect of hydrogen on temperature and species profiles

The oxidation of ammonia and ammonia-hydrogen systems was analyzed for mixtures diluted in N₂ at d=86 and 90% as a function of mixture inlet temperature and equivalence ratio (ϕ), at a fixed residence time (τ =0.21 s) under nearly atmospheric pressure (p=1.4 atm).

For the oxidation of NH_3/O_2/N_2 and NH_3-H_2/O_2/N_2 mixtures, the equivalence ratio ($\varphi)$ was defined

as follow:

$$\phi = \frac{H/0}{(H/0)_{\text{stoich}}}$$

where H/O indicates the ratio between the molar fraction of hydrogen atoms in both the fuels and the molar fraction of oxygen atoms in the O₂, whereas H/O_{stoich} represents the stoichiometric hydrogen to oxygen ratio based on both the reactions $4NH_3+3O_2=2N_2+6H_2O$ and $2H_2+O_2=2H_2O$.

This approach was chosen to compare the behavior of the NH_3/O_2 and NH_3-H_2/O_2 mixtures while keeping constant the overall mixture equivalence ratio. According to the given definition, the O_2 concentration changes preserving the overall mixture equivalence ratio.

The effect of H_2 was evaluated by changing the parameter R, defined as the mole fraction of H_2 on the total moles of fuels, according to the following equation:

$$R = \frac{H_2}{NH_3 + H_2}$$

In particular, R was changed from 0.05 to 0.15 with a step of 0.05. The explored operative conditions are summarized in the Table 8.

Conditions	Symbols	Range
Inlet temperature	Tin	900-1350 K
Equivalence ratio	φ	0.4-1.6
Residence time	τ	0.21 s
Pressure	Р	1.4 atm
Dilution level	d	86, 90% N ₂
Ratio H ₂ /(H ₂ +NH ₃)	R	0, 0.05, 0.10, 0.15

*Table 8. Operative conditions for the experimental tests for NH*₃-H₂ *mixtures.*

First, the mixtures diluted at 90% in N₂ were considered. Figure 35, Figure 36 and Figure 37 show the temperature increment ΔT and the O₂, H₂ and NO profiles as a function of T_{in}, at ϕ =0.8, 1.0 and 1.2, respectively, parametrically changing R (0, 0.05,0.1, 0.15).



Figure 35. Temperature and species profiles as a function of T_{in} , at $\phi=0.8$ and R=0, 0.05, 0.10, 0.15, diluted at 90% in N_2 .

For ϕ =0.8 and R=0 (Figure 35a, green squares), ΔT increases monotonically with T_{in}, then it abruptly increases for T_{in}=1270K. This temperature marks the shift from the low-intermediate to high temperature regime. Herein, this T_{in} will be indicated as T_{HT}. In addition, the low and intermediate regimes, previously defined, are herein considered together for simplicity.

Afterwards, ΔT reaches a maximum value (about 55K). Congruently with the ΔT profile, the O₂ concentration (Figure 35b) decreases with T_{in} and reaches the full-conversion value for T_{in}>1270K. The H₂ and NO profiles have the peculiar non-monotonic trend. In particular, the H₂ concertation (Figure 35c) increases from 0 up to a maximum of 0.06% at T_{in}=1250K, afterwards it decreases starting from T_{in}=1270K. On the other hand, NO concentration (Figure 35d) increases up to 130ppm at T_{in}=1130K, then, for T_{in}=1130-1270K, it decreases down to a minimum value equal to 40ppm. Then, it increases again up to 50ppm at T_{in}=1320K.

When part of NH₃ is replaced with H₂, while keeping constant ϕ , the system reactivity is slightly promoted, as shown by the ΔT and O₂ profiles. In fact, ΔT becomes higher, proportionally to the H₂ content, and T_{HT} decreases from 1270K (R=0) to 1260K, 1220K and 1210K for R=0.05, 0.10 and 0.15, respectively.

NO profiles have similar non-monotonic trends, independently of the H_2 mixture content. For T_{in} lower than T_{HT} , the NO concentration decreases by increasing the H_2 content. For higher temperatures, the NO concentration increases with the H_2 initial concentration, since the H₂ boosts the formation of OH radicals, thus promoting the NH₃ kinetic routes to NO formation.

For R=0.05, 0.10 and 0.15, the H₂ profiles behave similarly, as they decreases monotonically from the initial value down to 0. In particular, the H₂ profiles overlap from T_{in} >1250K, independently of the initial H₂ content.



Figure 36. Temperature and species profiles as a function of T_{in} , at $\phi=1.0$ and R=0, 0.05, 0.10, 0.15, diluted at 90% in N_2 .

The stoichiometric and fuel-rich mixtures (Figure 36 and Figure 37, respectively, green squares) exhibit oxidation behaviors similar to the fuel-lean condition for low-intermediate temperatures. Small differences can be observed for T_{HT} , that is equal to 1260K at ϕ =1 and 1250K at ϕ =1.2. The NO (Figure 36d and Figure 37d) profiles show the same non-monotonic trend for T_{in} <T_{HT}. In particular, NO profiles at ϕ =1 and 1.2 have a relative peak at T_{in} =1130K, with a concentration equal to 120ppm, lower than the one detected at ϕ =0.8. For higher temperatures, at the stoichiometric condition, NO profile has an increasing trend with T_{in} , and NO concentration increases up to 40ppm at 1320K, while at fuel-rich condition, NO concentration approaches a plateau value equal to 20ppm.

Prior to T_{HT} , the H₂ profiles (Figure 36c and Figure 37c) increase up to a plateau concentration, equal to 0.1% at ϕ =1 and 0.17% at ϕ =1.2. For higher T_{in} , at ϕ =1 the H₂ concentration increases and reaches a constant value equal to 0.21%, while in case of ϕ =1.2, it increases with T_{in} up to 1% at T_{in} =1320K.

The addition of H_2 to the stoichiometric and fuel-rich conditions provides results similar to the fuel-lean case in terms of mixture reactivity, as it shifts T_{HT} to lower T_{in} .

For higher temperatures, at ϕ =1.0, NO increases with the initial H₂ concentration, while at ϕ =1.2 NO decreases to a minimum value equal to 20ppm, independently of R. A different behavior was found for the NO profiles for lower temperatures. As a matter of fact, at ϕ =1, for T_{in}<1070K the NO concentration increases with R, while this trend is inverted for T_{in}=1070-1260K. At ϕ =1.2, the NO concentrations at different R are almost coincident, afterwards they exhibit a decreasing trend with R.



Figure 37. Temperature and species profiles as a function of T_{in} , at $\phi=1.2$ and R=0, 0.05, 0.10, 0.15, diluted at 90% in N_2

Finally, for the stoichiometric and fuel-rich mixtures, the H₂ profiles at R=0.05, 0.10 and 0.15 decrease to a relative minimum, prior T_{HT}. Therefore at ϕ =1, they increase for higher temperatures and reach a plateau, independently of R, while at ϕ =1.2, the H₂ profiles exhibit a growing trend and the concentrations increase with R.

Summarizing the previous experimental results, under the explored operating conditions, NH₃ oxidation process takes place through the different regimes, previously identified, depending on the inlet temperatures. Such regimes are only slightly affected by the mixture compositions (within the range ϕ =0.8-1.2) and hydrogen addition (within the range R=0-0.15).

Hydrogen moderately accelerates NH_3 oxidation, reducing the T_{HT} by about 50K at R=0.15. On the other hand, within the low-temperature regime, it can be observed that H_2 consumption is considerably slowed down by the NH_3 itself, as it is expected H_2 would be fully converted for the explored temperature window. This effect will be deeply discussed later.

4.8.2. Effect of H₂ on thermokinetic instabilities

As reported in the Paragraph 4.2, the transient study of the oxidation process of $NH_3/O_2/N_2$ mixtures (diluted at 86% in N₂) allowed to identify dynamic combustion behaviors during the transition from the low-intermediate to the high-temperature regime. To characterize the effect of H₂ on thermo-kinetic instabilities, the experimental results were replicated at d=86% varying the H₂ content in the reference mixture (R=0, 0.05, 0.1, 0.15). Results at R=0.15 are not discussed herein since no instabilities were detected. The experimental tests were replicated for many values of ϕ , up to draw-up experimental maps of behavior in the plane T_{in}- ϕ .

Figure 38 shows the map in the ϕ -T_{in} plane were dynamic behaviors were observed. In particular, the colored areas identify periodic oscillations while the striped-background areas the damped ones.

For the case of pure NH₃ (R=0, green area), the lower temperature boundary for the damped oscillations region is equal to $T_{in}=1250K$, independently of ϕ , while the high temperature limit changes considerably with ϕ . In particular, for $0.5 \le \phi \le 0.9$ it shifts to higher T_{in} as ϕ increases, then it decreases for $0.9 < \phi < 1$ and instabilities disappear for fuelrich conditions. Also periodic oscillation were detected. The area of periodic instabilities is restricted to small temperature and ϕ windows, namely $T_{in}=1255-1260K$ and $\phi=0.55-0.58$, hence the detection of such phenomenologies is only possible by adopting very tight $\Delta\phi$ and ΔT steps.



Figure 38. Experimental maps of behaviors as a function of T_{in} and ϕ , for NH₃-H₂/O₂/N₂ mixtures, diluted at 86% in N₂ (color area=periodic oscillations, area filled with lines=damped oscillations). Figure insets: examples of damped and periodic oscillations.

Increasing R, the dynamic regimes area shifted towards lower T_{in} and extend in a narrower ϕ range.

At R=0.05 (red area), the lower temperature boundary is equal to T_{in} =1230K for $0.65 \le \phi \le 1$. The high temperature limit increases from 1230K at ϕ =0.66 up to 1255K at ϕ =0.9, then it decreases to 1250K at the stoichiometric condition. Periodic oscillations are detected within a limited rectangular-shaped area at T_{in} =1230-1235K and ϕ =0.66-0.69. No oscillations are found for fuel-rich conditions.

At R=0.10 (blue area), the damped oscillations are confined in T_{in} =1210-1220K and ϕ =0.8-1, in particular they persist for a wider T_{in} range (1210-1230K) at around ϕ =0.9, as for R=0 and 0.05.

Examples of both the dynamic phenomena are reported in the insets of Figure 38. The inset "a" shows damped oscillations. The amplitude decreases in time, while the frequency increases up to 4Hz, as the average T_r increases. The oscillations extinguish as T_r approaches 1320K. When the average T_r stays within 1310-1320K, oscillations persist in time (inset "b") with a characteristic oscillation frequency of 2Hz.

In Paragraph 4.2, further transitional regimes were defined with respect to T_r . In particular, it was shown that the transition from the low-intermediate temperature to the HT may occur through a Lower Reactivity (LR) regime, where the temperature increment defines a low-slope trend, followed, in dependence ϕ , by a stable or unstable dynamic regime (DR), characterized by a steeper slope, towards the steady state condition. The T_r range were instabilities where detected are independent of ϕ and T_{in} . To highlight these characteristic features of this transient mode, in Figure 39 the temporal temperature profiles are reported for ϕ =0.8 and R=0, 0.05, 0.1, with the identification of the LR and DR regimes (flags).



Figure 39. Experimental T_r profiles in time at ϕ =0.8 and R=0 (T_{in} =1270K, green line), R=0.05 (T_{in} =1250K, orange line) and R=0.1 (T_{in} =1230K, red line).

For pure NH₃, T_r increases in time up to 1300K, passes through a LR regime up to 1310K, then, damped oscillations occur and they extinguish at T_r =1320K. Afterwards, T_r increases up to the steady state condition.

These transitional regimes slightly change with the H_2 mixture content. The LR starts at $T_r=1280$ K up to $T_r=1290$ K for R=0.05, then the DR occurs in-between 1290-1300K. For R=0.1, the LR establishes for $T_r=1260-1270$ K, while the DR in the range 1270-1280K.

Numerical simulations were performed with Zhang, Nakamura, Shrestha and Glarborg mechanisms to investigate their capability to predict the NH₃-H₂ interaction.

For the sake of briefness, the comparison among the experimental data and numerical profiles is presented only at ϕ =0.8, d=90% and R=0.1. The general agreement among models and experimental results is the same for the stoichiometric and fuel-rich conditions.

Results are reported in Figure 40. The ΔT and O₂ profiles show Zhang mechanism is able to reproduces satisfactorily the experimental data, even though it predicts periodic oscillations at T_{in}=1230-1240K, not experimentally detected under these operating conditions. The other schemes can predict the high-temperature experimental behavior, but suggest faster reactivity for low-intermediate T_{in}. For this condition, Nakamura and Shrestha mechanisms do not predict the occurrence of instabilities.



Figure 40. Numerical predictions vs experimental data for NH_3 - $H_2/O_2/N_2$ mixture at ϕ =1.0, R=0.10, d=90%.

With reference to the H₂ profile (Figure 40c), Nakamura mechanism is able to reproduce the data for the intermediate T_{in} window, however it underestimates the H₂ concentration for low temperatures. Shrestha, Glarborg and Zhang models overestimate the H₂ conversion for T_{in} <1270K.

As for the case at R=0, disagreements exist in the NO prediction (Figure 40d), for the whole T_{in} range.

The performances of the chosen mechanisms to predict the experimental data were further tested against the maps of behaviors. To this aim, simulations were performed in time, by changing R, ϕ and T_{in}, for a mixture dilution level equal to 86%. Both damped and periodic oscillations were identified and reported on the ϕ -T_{in} map, adopting the same legend, namely the colored areas for periodic oscillations and the striped-background area for damped instabilities. The maps at different R are reported in Figure 41. The maps are overlapped on the same diagram for Glarborg and Zhang mechanisms, while the same are distinguished in three different figures for Nakamura and Shrestha models, in order to simplify the reading.

According to Glarborg model (Figure 41a), the oscillation region at R=0 extends in the range ϕ =0.4-1. The low temperature boundary is located at T_{in}=1200K for each ϕ , while the high temperature one is more sensitive to ϕ . In particular, the extinction temperature for the oscillation increases as ϕ increases up to 1300 at ϕ =0.9 and then it decreases down at ϕ =1. Two small regions of damped oscillations delimitate the periodic instabilities area at lower and higher T_{in}. Increasing R, the high-temperature damped oscillations areas disappear. The regions are shifted towards lower T_{in} and confined within a tighter ϕ -range (in particular ϕ =0.6-1 at R=0.05 and ϕ =0.7-0.95 at R=0.10), nonetheless, the shape of the area is preserved, as well as its extension at ϕ =0.9.

The maps of behaviors according to Zhang model (Figure 41b) are almost similar to the Glarborg ones. The oscillations region at R=0 has a low-temperature boundary at T_{in} =1255K. It occurs in the range T_{in} =1270-1280K for ϕ =0.4-0.9 and exhibits a "noselike" shape around $\phi=0.8-1$, in particular the temperature where oscillations end is maximum at $\phi = 0.9$ (T_{in}=1340K). The damped oscillation area has a rectangular shape and it is located within T_{in} =1280-1290K and ϕ =0.4-0.9. As R increases, oscillation areas move towards lower T_{in} and extend in a narrower ϕ -range, while maintaining the same shape. On the other hand, the damped oscillations regions become slightly wider as R increases. The maps of behaviors by Nakamura mechanism (Figure 41c) are quite different from those previously illustrated. At R=0, the map extends in a wider T_{in}-range (T_{in}=1100-1390K) and in a narrower ϕ -range (ϕ =0.8-1) with respect to the other mechanisms. In this region, an extension of the map with respect to T_{in} is identifiable for $\phi=0.9$. Also damped oscillations persist for a larger T_{in} range, namely 1050-1100K for ϕ =0.8-1. In case of NH₃-H₂ mixtures, no oscillations are predicted at the stoichiometric condition, as the areas are restricted within a narrower ϕ -range, namely ϕ =0.80-0.95. At R=0.05, the periodic oscillations and damped oscillations regions lay in-between T_{in}=1100-1350K and T_{in}=1050-1100K, respectively, while at R=0.1 they are located within T_{in}=11351300K (periodic oscillations) and T_{in} =1050-1135K (damped oscillations). The extension of the map at ϕ =0.9 still persists for R=0.05 and 0.10.

Finally, the maps according to Shrestha mechanism are showed in Figure 41d. At R=0, the periodic oscillations are predicted around T_{in} =1285-1300K and ϕ =0.7-1. The damped oscillations area is larger, as it extends for T_{in} =1260-1285 and ϕ =0.7-1. In this case, the areas have a more "regular" shape with respect to the other models, in particular, the high temperature boundary does not exhibit a stronger dependence on the equivalence ratio. At R=0.05, the instabilities regions noticeably reduce. At ϕ =1, the periodic oscillations are replaced by the damped ones, in fact the periodic oscillations area takes a rectangular shape within T_{in} =1270-1250K and ϕ =0.85-0.95. For R=0.1, the periodic oscillations disappear, and only a small region of damped oscillations persists around ϕ =0.85-0.90 and T_{in} =1260-1270K.



Figure 41. Numerical maps of behaviors as a function of T_{in} and ϕ , for NH₃-H₂/O₂/N₂ mixtures, diluted at 86% in N₂ (color-filled area=periodic oscillations, line-filled area=damped oscillations).

Comparing the numerical maps with the experimental results, it must be highlighted that the calculated periodic oscillations areas are significantly larger than the experimental ones, whilst the calculated damped oscillation regions are tighter than the experimental ones. In additions, the shape and the extension of each area, as well as the amplitude, shape and frequency of the temperature oscillations, change mechanism by mechanism. As an example, in Figure 42 it is possible to compare the frequency and amplitude of temperature oscillations at ϕ =0.9 and R=0 for all the selected mechanisms. The figure

shows the ΔT profiles as a function of T_{in} . The profile splits in two lines when periodic oscillations occur: the upper line represents the maximum ΔT during the oscillation period $(\Delta T_{max}=T_{max}-T_{in})$ and the lower line is the minimum ΔT during the oscillation period $(\Delta T_{min}=T_{min}-T_{in})$. The frequency diagram is reported in the corresponding figure inset for each mechanism.

Apart of the different T_{in}-range where instabilities occur, the graphs highlight the discrepancies among the mechanisms in the description of oscillations amplitude and frequency. For instance, the maximum oscillation amplitude according to Glarborg model is around 350K, with frequencies from 0 up to 40Hz, while the maximum oscillation amplitude for Zhang mechanism is around 80K and the frequency does not exceed 20 Hz.



Figure 42. Numerical T_r profiles as a function of T_{in} , at $\phi=0.9$ and R=0.

Nonetheless, beyond these discrepancies, some peculiar features of the experimental maps are described by the models. Indeed, the overall effect of H_2 is predicted, since the simulations suggest that the addition of H_2 shifts the oscillation regions towards lower $T_{\rm in}$ and the areas become smaller and smaller as the H_2 initial concentration increases.

In addition, to some extent, Glarborg, Nakamura and Zhang models reproduces the shape of the low and high temperature boundaries of the areas, since the numerical maps show that the onset of the oscillations is almost independent of ϕ , while the end of the dynamic phenomena is mostly affected by the mixture stoichiometry, in particular oscillations persist for a wider T_{in}-range around ϕ =0.9.

4.9. The inhibiting effect of ammonia on H₂ oxidation

In this section, the plausible role of ammonia as third-body species (discussed in the Paragraph 2.2) in three body reactions is assessed through a deductive analysis. The deductive nature of this study comes from an indirect evaluation of the ammonia effects on H_2 -O₂ chemistry in the JSFR, while parametrically changing the ammonia concentration. Results are then compared with experimental evidences for mixtures partially diluted in water.

Specifically, experimental tests were first realized for $H_2/O_2/Ar$ and $H_2/O_2/N_2$ mixtures as reference cases under MILD operative conditions. Successively, the oxidation process was analyzed replacing Ar or N_2 with variable amounts of water or ammonia.

The choice of Ar as a diluent agent was twofold: former, in kinetic schemes it has a lower collisional efficiency with respect to N_2 , thus strong colliders third-body effects may be emphasized; latter, for mixtures partially diluted in NH₃, it allows to indirectly check the ammonia reactivity by simply measuring N_2 .

The mixture equivalence ratio (ϕ) was defined as:

$$\phi = \frac{(H_2/O_2)}{(H_2/O_2)_{stoich}} = \frac{1}{2}(H_2/O_2)$$

Ammonia was not considered within the definition of the mixture equivalence ratio, but ideally treated as an inert species. Indeed, the results reported in the Paragraphs 4.1-4.8 show NH₃ conversion under oxidative conditions is negligible for T<1200K. This aspect was further verified by measurement of N₂ in the exhausted gases for the H₂/O₂/Ar mixture.

Conditions	Range
Inlet temperature (T _{in})	800-1250 K
Equivalence ratio (Φ)	0.5
Residence time (τ)	τ=0.5 s
Pressure	1.2 atm
Global dilution level (d)	94% Ar or N ₂
NH ₃ dilution	2, 5, 7.5, 10 %
H ₂ O dilution	5, 10, 15, 20 %

The experimental conditions are summarized in Table 9.

Table 9. Operative conditions for the experimental tests performed for H_2 - O_2 mixtures.

4.9.1. H₂/O₂/Ar/H₂O mixture

The first experimental tests were realized with fuel-lean (ϕ =0.5) H₂-O₂/Ar-H₂O mixtures with an increasing concentration of water (5%, 10%, 15%, 20%), to show the water interaction on the H₂-O₂ chemistry as a third-body species, as reported in [15]. The overall mixture dilution level is 94%. The temperature increase (Δ T= T_r-T_{in}) along with the O₂ and H₂ concentrations as a function of T_{in} are reported in Figure 43.



Figure 43. Temperature, O_2 and H_2 profiles as a function of the inlet temperature for fuel-lean H_2 - O_2 mixtures (ϕ =0.5) at fixed τ =0.5 s and p=1.2 atm, diluted in Ar- H_2O at 94% with an increasing concentration of H_2O (5%, 10%, 15%, 20%). Open symbols identify the occurrence of temperature oscillations. Cross symbols identify pre-ignition within the premixing chamber.

For the H₂/O₂/Ar system, the mixture starts reacting at T_{in} =850K (Figure 43a) with the establishment of thermo-kinetic periodic temperature oscillations in time, recognizable for T_{in} =850-880K (indicated by empty symbols), while H₂ and O₂ concentrations decrease (Figure 43b-c). Within the dynamic instabilities range, their concentration is time-averaged. At higher temperatures, pre-ignition within the premixing chamber (cross symbols) is observed, thus data are not trustworthy. For mixtures partially diluted in water, the system reactivity shifts towards higher T_{in} as much as H₂O concentration is increased. For H₂O=5%, the onset of reactivity is recognizable at T_{in} =860K, followed by temperature oscillations in the range 860K< T_{in} <900K. At T_{in} =915K, dynamic phenomenologies disappear and the system reaches a steady stationary condition, with a temperature increment of 25K. H₂ and O₂ fully convert in relation to the mixture equivalence ratio. For T_{in} >950K, experimental data have to be discarded since pre-ignition phenomena occur in the premixing section of the JSFR.

For the systems H_2 -O₂/Ar-H₂O (10%) and H_2 -O₂/Ar-H₂O (15%), the onset of reactivity occurs at T_{in}=890K and 900K, respectively. The instabilities are also shifted at higher T_{in}

and span over an increasingly smaller range as the water content increases. For water concentration higher than 20%, the onset of system reactivity occurs at T_{in} =900K and oscillatory phenomenologies are no longer detected. The temperature increase at the final stationary steady state slightly decreases with water content.

According to [11], such effects have to be correlated to the enhanced role of reaction $H+O_2+M=HO_2+M$, in virtue of the high water third body collisional efficiency, that suppresses the reactions $H+HO_2=OH+OH$ and $H+O_2=OH+O$ as OH radical sources, thus decreasing the overall mixture reactivity. In this context, it is worth noting that Ar has a very small third body collisional efficiency, being a monoatomic species [100–102,135], thus the comparison with mixtures partially diluted in water is realized with the aim to strongly emphasize the role of third-molecular reactions.

4.9.2. H₂/O₂/Ar/NH₃ mixture



Following the same approach, further tests were realized for H_2 -O₂/Ar-NH₃ mixtures for different NH₃ amount (2%, 5%, 7.5%, 10%). Results are reported in Figure 44.

Figure 44. Temperature, O_2 and H_2 profiles as a function of the inlet temperature for fuel-lean H_2 - O_2 mixtures (ϕ =0.5) at fixed τ =0.5 s and p=1.2 atm, diluted in Ar-NH₃ at 94% with an increasing concentration of NH₃ (2%, 5%, 7.5%, 10%). Open symbols identify the occurrence of temperature oscillations. Cross symbols identify pre-ignition within the premixing chamber.

Similarly to $H_2/O_2/Ar-H_2O$ mixtures, when even small percentage of NH₃ is added to the mixture, H₂ and O₂ consumption is significantly shifted toward higher T_{in} with respect to the reference case (no NH₃). In particular, for H₂/O₂/Ar-NH₃(2%), the onset of system reactivity occurs at T_{in}=875K, as the reactor temperature starts increasing while H₂ and O₂ consuming. For H₂/O₂/Ar-NH₃(5%), H₂/O₂/Ar-NH₃(7.5%), such a condition is

identifiable respectively for T_{in} =875K and 950K. Also for H₂/O₂/Ar-NH₃(10%), the onset of mixture reactivity occurs at about T_{in} =950K. It is worth noting that temperature oscillations are not detected for any of the H₂/O₂/Ar-NH₃ mixtures. Ammonia seems to have an effect on H₂-O₂ oxidation chemistry significantly larger than the one detected for water, even for very low ammonia concentration. Moreover, it also seems that an increase of ammonia percentage does not change much the system behavior at least until relatively large concentrations of NH₃. A paramount exemplification of these statements is given by the H₂ profiles vs T_{in} (Figure 45) for H₂/O₂/Ar-NH₃(2%) and H₂/O₂/Ar-H₂O(20%). H₂ concentration is considered as representative of the overall system reactivity. It is interesting to note that there is not a significative difference between the two considered profiles, since a concentration of ammonia of 2% equals the effect of a concentration of water of 20%.

These observations stimulate the research of the actual interaction of the ammonia molecules with the H_2/O_2 chemistry.



Figure 45. Comparison between H_2 profiles for fuel-lean H_2 - O_2 mixtures (ϕ =0.5) diluted in Ar- $H_2O(20\%)$ and Ar- $NH_3(2\%)$, at fixed τ =0.5 s and p=1.2 atm.

The ammonia conversion was indirectly verified by measuring N_2 and NO concentrations at the outlet of the reactor for all the mixtures diluted in Ar-NH₃, due to difficulties to measure NH₃ with enough precision. In Figure 46, N₂ profiles from the oxidation of H₂/O₂/Ar-NH₃, for all the NH₃ concentrations considered herein, are reported.

 N_2 concentration, for an inlet NH_3 concentration equal to 2%, is almost zero for T_{in} <920K and increases up to 0.3% at T_{in} =950K. For the mixtures with higher NH_3 concentrations, N_2 profiles have similar trends and N_2 is released for T_{in} >1000K. These results suggest that ammonia remains for the most unconverted under the investigated conditions, namely NH_3 oxidation and/or decomposition have a small impact on H_2 and O_2 profiles.



Figure 46. N₂ profiles as a function of the inlet temperature for fuel-lean H₂-O₂ mixtures $(\phi=0.5)$ at fixed $\tau=0.5$ s and p=1.2 atm, diluted in Ar-NH₃ at 94% with an increasing concentration of NH₃ (2%, 5%, 7.5%, 10%). Cross symbols identify pre-ignition within the premixing chamber.

4.9.3. H₂/O₂/N₂/NH₃ mixture

The experimental tests were extended to $H_2/O_2/N_2$ -NH₃ mixtures in order to verify the ammonia role as an inhibiting agent on the H₂/O₂ chemistry in different bath gases. N₂ was chosen as a diluent species since it may decrease the H₂ reactivity, in virtue of a slightly higher heat capacity and third-body collisional efficiencies in third-molecular reactions with respect to Ar, thus it can amplify the effect of NH₃ on the H₂ oxidation chemistry. In addition, without considering implications in NO_x formation chemistry (negligible for the considered temperature range, as reported in [50]), it can be considered as an inert species. Therefore, tests were realized with lean (ϕ =0.5) H₂-O₂/N₂-NH₃ mixtures with an increasing concentration of NH₃ (5%, 10%, 15%, 20%). Results are showed in Figure 47. For the mixture diluted in N₂, the temperature profile starts increasing at T_{in}=880K where an oscillatory behavior (empty circles) was observed. Correspondingly, O₂ and H₂ concentrations abruptly decrease at T_{in}=880K. Suddenly, after this temperature, the system becomes stable (at T_{in}=890K) with a temperature increase, Δ T, slowly declining with T_{in} from 25K down to 20K. For T_{in}>950K, mixture ignition takes place within the premixing chamber (cross symbols).

Generally, in presence of NH₃, the H₂-O₂ reactivity of mixtures drastically decreases. Referring to the mixture with 2% of NH₃, H₂ decreases monotonically as a function of T_{in} and its conversion is around 50% at T_{in}=975K, whereas, for the mixture without ammonia, H₂ is completely consumed. As the NH₃ concentration increases, such a retarding effect is emphasized. For the NH₃ concentration equal to 10%, the reference mixture starts reacting at T_{in}=950K and slightly consumes as T_{in} increases.



Figure 47. Temperature, O_2 and H_2 profiles as a function of the inlet temperature for fuel-lean H_2 - O_2 mixtures (ϕ =0.5) at fixed τ =0.5 s and p=1.2 atm, diluted in N_2 - NH_3 at 94% with an increasing concentration of NH_3 (2%, 5%, 10%). Open symbols identify the occurrence of temperature oscillations. Cross symbols identify pre-ignition within the premixing chamber.

Since NH_3 concentration is not measured for these experimental campaigns, NH_3 conversion could not be quantitatively evaluated. However, further tests were carried out at the same conditions by simply removing the H_2 from the mixture (not reported here). Results suggested that the reactivity of the mixture was negligible for the investigated T_{in} range.

In order to fully characterize the effects of NH₃ on the H₂/O₂ chemistry, further tests were realized at a fixed inlet temperature (T_{in} =970K) while parametrically increasing the NH₃ up to a concentration of 20%. Tests were performed for these conditions since NH₃ conversion is negligible, as deducible from Figure 46. The same tests were realized with both Ar and N₂ as bath gases. H₂ and O₂ are reported as illustrative species of H₂/O₂ chemistry. Figure 48a and b show the O₂ and H₂ concentrations respectively for the mixture H₂-O₂/Ar-NH₃ and H₂-O₂/N₂-NH₃. In the same pictures, the heat capacities (c_p)

of the mixtures H_2 -O₂/Ar-NH₃ and H_2 -O₂/N₂-NH₃ are reported as a function of the ammonia concentration in order to clearly address the nature of these effect.



Figure 48. Comparison between O_2 and H_2 profiles as a function of the inlet temperature for fuel-lean H_2 - O_2 mixtures (ϕ =0.5) diluted in Ar-NH₃ and N₂-NH₃, at fixed τ =0.5 s and p=1.2 atm.

In case of both H₂-O₂/Ar-NH₃ and H₂-O₂/N₂-NH₃ mixtures, O₂ and H₂ increase with NH₃ content until a 10% concentration of NH₃ is reached. At higher NH₃ concentrations, O₂ and H₂ concentrations remain constant and very close to their inlet values, thus suggesting that NH₃ may completely damp hydrogen reactivity. This "saturation" effect recalls the "fall-off" pressure dependence of reaction rates from the low to the high-pressure limits, suggesting that third-molecular reactions may play a crucial role in the H₂ oxidation chemistry in presence of ammonia. In addition, the comparison between H₂ and O₂ profiles for H2-O2/Ar-NH3 and H2-O2/N2-NH3 mixtures at Tin=970K clearly shows that, independently of the main diluent, namely Ar or N₂, the system reactivity is completely controlled by ammonia, since H₂ and O₂ profiles are almost identical for the two systems. The cp of the H2-O2/Ar and H2-O2/N2 mixtures are respectively equal to 5 J/mol K and 8 J/mol K, then they increase with the ammonia concentration up to 7 and 9 J/mol K for an ammonia concentration equal to 20%. The overlapping of the H₂ and O₂ concentrations for the two reference mixtures suggests also that the thermal properties of the mixtures can be neglected to explain the effect of ammonia on the H₂/O₂ chemistry, thus kinetic effects should be called into question.

4.9.4. Numerical results

Numerical simulations were realized for the system $H_2/O_2/Ar$ and $H_2/O_2/N_2$ with different amount of NH₃, using the following kinetic mechanisms: Zhang, Glarborg, Konnov and Nakamura.

As a first step, preliminary simulations were realized considering the systems $H_2/O_2/Ar$ without ammonia in order to verify the capability of the chosen kinetic mechanisms to reproduce the experimental evidences without considering the ammonia chemistry.

Figure 49 shows the comparison between experimental data and numerical profiles for the H_2/O_2 mixtures diluted in Ar (Figure 49a-c) and N₂ (Figure 49d-f). The temperature

increment ΔT along with the H₂ and O₂ concentrations are reported as a function of T_{in} for the two reference mixtures.

The numerical results suggest that Zhang, Nakamura and Konnov mechanisms provide the same temperature and species profiles, while Glarborg scheme predicts an overall lower reactivity with respect to the other schemes and experimental data.



*Figure 49. Comparison between experimental and numerical profiles for the mixtures diluted in Ar (a-c) and N*₂ (*d-f*).

For the mixtures diluted in Ar (Figure 49a-c), the numerical temperature profiles by Zhang, Nakamura and Konnov reproduce satisfactorily the experimental data. Small discrepancies are recognizable only for the temperature range where instabilities occur (dashed lines). In fact, models suggest that temperature oscillations come up within T_{in} =850-890K, while the experimental evidences highlight oscillations for a narrower temperature range, namely T_{in} =850-870K. Similarly, numerical O₂ and H₂ profiles by Zhang, Nakamura and Konnov start to decrease at T_{in} =850K and a complete conversion is predicted for T_{in} >890K, thus reproducing the experimental data outside the dynamic regime. According to Glarborg scheme, the temperature profile starts to increase at T_{in} =960K and instabilities occur for T_{in} =870-910K. Congruently, O₂ and H₂ start to decrease for T_{in} >860K and are completely consumed for T_{in} >910K.

Zhang, Nakamura and Konnov mechanisms provide better predictions than Glarborg scheme also for the oxidation of the mixture diluted in N₂ (Figure 49d-b). In fact, according to Zhang, Nakamura and Konnov mechanisms, temperature profile starts increasing at T_{in} =880K and temperature oscillations occur for T_{in} =890-920K. On the other hands, Glarborg model suggest that the onset of reactivity occurs at 890K, with dynamic regimes within T_{in} =900-930K. H₂ and O₂ profiles decrease congruently with temperature profiles.

Secondly, numerical simulations were realized for the mixtures $H_2/O_2/Ar-NH_3(5\%)$ and $H_2/O_2/Ar-NH_3(10\%)$, in order to evaluate the sensitivity of detailed mechanisms to ammonia chemistry.

Figure 50 shows the experimental and numerical profiles for the mixture diluted in Ar-NH₃(5%) and Ar-NH₃(10%). The temperature increment ΔT along with the H₂ and O₂ concentrations are reported as a function of T_{in} for the two reference mixtures.

In general, the selected kinetic mechanisms behave similarly. For instance, considering the case with 5% of NH₃, the numerical temperature profiles (Figure 50a) start to increase at T_{in} =830K (according to Konnov and Zhang schemes) or T_{in} =840K (according to Nakamura and Glarborg models). For this operative condition, the agreement with the experimental ΔT is not very good, as the experimental tests suggest temperature starts increasing for T_{in} =870K.

In addition, the numerical temperature profile exhibits a sharp increment in proximity of the conditions where the mixture starts to react, namely for T_{in} =830-840K for Zhang and Konnov mechanisms and T_{in} =840-850K for Glarborg and Nakamura ones. Afterwards, increasing T_{in} , ΔT rises with a lower slope for all the mechanisms. Such a trend was not experimentally observed. Congruently with the temperature profiles, the models overpredict the O₂ and H₂ (Figure 50b-c) conversion with respect to the experimental data for T_{in} <1000K and provide higher concentrations for higher temperatures (T_{in} >1000K).



Figure 50. Comparison between experimental and numerical profiles for the mixtures diluted in Ar-NH₃(5%) and Ar-NH₃(10%).

The discrepancy between experiments and simulations increases with the NH₃ content. For instance, in case of 10% of NH₃ (Figure 50d-f), the O₂ and H₂ experimental profiles start to decrease at T_{in} =950K while the simulated ones decrease for T_{in} >880K. In addition, Konnov and Nakamura mechanisms predict a non-monotonic H₂ profile, as for T_{in} >970K

 H_2 concentration starts increasing due to NH_3 decomposition. The change of the slopes of the temperature and species numerical profiles is less pronounced for the case Ar- $NH_3(10\%)$ with respect to the Ar- $NH_3(5\%)$ mixture.

4.10. A comprehensive kinetic analyses of NH₃-H₂ interaction under low-intermediate temperatures

The results illustrated in the Paragraphs 4.8 and 4.9 bring to the light some peculiarities of NH_3-H_2 interactions for low-intermediate temperatures.

Specifically, the experiments on NH₃-H₂/O₂/N₂ mixture highlight that:

- H₂ slightly enhances the reactivity of the system.
- Increasing the H₂ content in the inlet mixture, the dynamic regimes areas in the T_{in} - ϕ plane shift towards lower T_{in} and extend in a narrower ϕ range. Instabilities disappear for H₂ content higher than 15%.
- NH₃ partially delays the H₂ conversion, thus limiting its role as "fuel-enhancer".

On the other side, considering the H_2/O_2 mixtures diluted in N_2 -NH₃ and Ar-NH₃ the most relevant outcomes are:

- NH₃ has a strong inhibiting effect on H₂ oxidation, since the onset of the system reactivity is shifted towards higher inlet temperatures as the ammonia concentration increases.
- Increasing ammonia content, the reactivity goes towards a "saturation" effect, with a lower variation on mixtures reactivity with an increase of ammonia concentration.

While the enhancing and stabilizing effect of H_2 on NH_3 oxidation was expected, as supported by several literature, the inhibiting role of NH_3 is a unique result related to the interaction of ammonia on the H_2 oxidation chemistry at temperature relevant for the H_2 oxidation chemistry itself. Indeed, the previous considerations contribute to conceive a plausible role of ammonia as a "strong" collider in ter-molecular reactions. This hypothesis is also supported by the physical/chemical properties of ammonia, because it has a high polarity and a dipole moment comparable to water. As matter of fact, the "strong" collider nature of water in the reaction $H+O_2+M=HO_2+M$ is commonly attributed to the very strong polar-polar interaction with HO_2 radical.

In order to understand the oxidation chemistry behind the NH₃-H₂ interactions, kinetic analyses were carried out.

First, the results are discussed for NH_3 - $H_2/O_2/N_2$ mixture, thus focusing on the enhancing effect of H_2 on NH_3 reactivity and its stabilizing role on thermo-kinetic instabilities (Paragraph 4.10.1).

Second, the kinetic analyses for the $H_2/O_2/N_2$ -NH₃ systems are presented, to clarify the inhibiting role of ammonia on H_2 oxidation (Paragraph 4.10.2).

4.10.1. Analyses of the oxidation chemical kinetics of NH₃-H₂/O₂/N₂ system

Flux diagrams and sensitivity analyses were performed for each of the selected mechanisms at ϕ =0.9 and d=86%, for pure ammonia (R=0) and for NH₃-H₂ mixture (R=0.1). For the HT regime, the reference temperature for the kinetic studies was fixed at T_{in}=1350K. For the LT regime, since all the mechanisms behave differently, the reference temperature was chosen at Δ T=5K.

Although the LT ammonia oxidation pathways changes mechanism by mechanism, all the models agree about the kinetic effect of H_2 on NH_3 oxidation. Therefore, since the Zhang mechanism is the most reliable under the explored operative conditions, it was selected for the detailed kinetic analysis.

First, the flux diagrams and sensitivity analyses are first briefly discussed at R=0 and $T_{in}=1250$ K and 1350K, in Figure 51 and Figure 52, respectively.

For each diagrams, the overall order of magnitude of the RR is reported in the legend. The arrow thickness is proportional to the RR value, reported in round brackets. Ammonia and nitrogen species are reported in black, H_2 while radicals from H_2/O_2 mechanism in red.

At 1250K, NH₃ is dehydrogenated to NH₂ according to the reaction NH₃+OH=NH₂+H₂O. The NH₂ radical is converted into products N₂ and NO through different channels. The main conversion pathways involve the formation of oxygenated intermediates, namely H₂NO and HNO, through the following reactions: NH₂+HO₂=H₂NO+OH, H₂NO+NH₂=HNO+NH₃, HNO+O₂=NO+HO₂. Alternatively, the NO formation may come through the H₂NO isomerization (H₂NO+M=HNOH+M), followed by the formation of N₂H_x species: HNOH+NH₂=N₂H₃+OH, N₂H₃+NH₂=H₂NN+NH₃, H₂NN+O₂=NO₂+NH₂ and NO₂+NH₂=NO+H₂NO.

The formed NO is involved in the DeNO_x pathways [87,114], namely the terminating reaction $NH_2+NO=N_2+H_2O$ or the branching reaction $NH_2+NO=NNH+OH$, followed by NNH decomposition to N₂ (NNH=N₂+H).

The formation of OH radicals is, for the most, dependent on the slow NH₃ conversion pathways through the reactions NH₂+HO₂=H₂NO+OH and NH₃+O=OH+NH₂. Even though it has a positive sensitivity coefficient, the reaction H+O₂=OH+O is too slow to provide a conspicuous OH production, because it is not supported by an adequate H radical formation. In fact, the reactions that promote the H formation exhibit positive sensitivity coefficients, such as N₂H₂+M=NNH+H+M, N₂H₃=N₂H₂+H, as well as the reaction H₂NO+NH₂=HNO+NH₃, that produces the HO₂ radicals responsible for the OH production.

Evidently, the DeNO_x reactions $NH_2+NO=NNH+OH$ and $NH_2+NO=N_2+H_2O$ have opposite effects on the mixture reactivity, as suggested by the sensitivity coefficients, since the former produces OH radicals and the latter is a terminating reaction.



Figure 51. Flux diagram and sensitivity analysis according to Zhang mechanism at $T_{in}=1250K$, R=0, d=86% in N₂. The reaction rates are proportional to E-8.

For higher temperatures, NH₃ oxidation is controlled by faster NH₂ routes, as reported in Figure 52.

The DeNO_x reactions still cover an important role but, in addition, NH₂ can be converted through the reactions: NH₂+OH=NH+H₂O, NH₂+O=HNO+NO and NH₂+NH=N₂H₂+H. The HNO formation and consumption reactions lead to the NO production, as discussed for the low-temperature oxidation. The NH reaction pathways, as well as the NNH decomposition, are responsible for the increment of the overall system reactivity, because they produce H and O radicals to sustain the high-temperature branching mechanism (H+O₂=OH+O, H₂O+O=OH+OH). In particular, the H radicals come from the reactions: NH+OH=HNO+H, NH+NO=N₂O+H, NH₂+NH=N₂H₂+H and NNH=N₂+H. As for the low-temperature, the reactions NH₂+NO=NNH+OH and H+O₂=OH+O have the highest sensitivity coefficients, while NH₂+NO=N₂+H₂O exhibits a negative T sensitivity coefficient.



Figure 52. Flux diagram and sensitivity analysis according to Zhang mechanism at $T_{in}=1350K$, R=0, d=86% in N₂. The reaction rates are proportional to E-7.

The effect of H_2 on the LT ($T_{in}=1050K$) and HT ($T_{in}=1350K$) oxidation pathways is reported in Figure 53 and Figure 54, respectively.

The LT flux diagram highlights that the most relevant interaction between NH₃ and H₂ oxidation chemistry is represented by the reaction $NH_2+H_2=NH_3+H$, that is the main consumption channel for both NH₂ and H₂. Indeed, the reaction $NH_3+OH=NH_2+H_2O$ acts as a "scavenger" for the OH radicals, thus inhibiting and delaying the direct H₂ oxidation through the reaction H₂+OH=H+H₂O and forcing H₂ to react with NH₂ radicals. On the other hand, the reaction $NH_2+H_2=NH_3+H$ boosts the H production, thus relieving it from the slower NH_2 oxidation pathways. As a consequence, the high temperature branching mechanism (H+O₂=OH+O) is fast enough to contribute to OH production, along with the reaction $NH_2+HO_2=H_2NO+OH$, thus promoting the system reactivity. These statements are further supported by sensitivity analyses. Indeed, the reaction $NH_2+H_2=NH_3+H$ has a positive sensitivity coefficient, as well as the reactions $H+O_2=OH+O$ and $NH_2+NO=NNH+OH$.

Given that the system reactivity is shifted at lower temperatures, the reaction $H+O_2+M=HO_2+M$ becomes competitive with $H+O_2=OH+O$, as suggested by the sensitivity analysis.

Apart from the reaction $NH_2+H_2=NH_3+H$, the main NH_2 oxidation pathways are not further affected by the presence of H_2 . The latter consideration is effective also for the HT regime, as showed by the flux diagram in Figure 54.



Figure 53. Flux diagram and sensitivity analysis according to Zhang mechanism at T_{in} =1050K, R=0.1, d=86% in N₂. The reaction rates are proportional to E-8.

Even though the reaction $NH_2+H_2=NH_3+H$ is no more effective at high temperature, H_2 has a substantial effect only on the branching mechanism, because it produces H radicals through the reaction $H_2+OH=H+H_2O$, downgrading the role of the NNH decomposition.



Figure 54. Flux diagram and sensitivity analysis according to Zhang mechanism at $T_{in}=1350K$, R=0.1, d=86% in N_2 . The reaction rates are proportional to E-7.

In order to understand the mechanism that leads the onset of instabilities, Reaction Rates analyses were run as a function of T_{in} , at R=0 and R=0.1. The diagrams in case of pure ammonia have been discussed in detail in the Paragraph 4.4. Herein, the case at R=0.1 is examined. For the sake of clarity, diagrams report only the main NH₂ reactions along with the branching mechanism.

At R=0.1 (Figure 55), the controlling reactions are almost the same for the LT and the HT regimes, identified in Figure 26. Nevertheless, the promoting effect of the reaction $NH_2+H_2=NH_3+H$ is evident for low-temperatures, as it enhances H radicals production. As a consequence, the role of the classical chain branching reaction is emphasized at lower temperatures, thus the overall system reactivity is increased and the system comes into the dynamic regime for low T_{in} with respect to the reference case. In addition, the higher concentration of H/OH in the radical pool allows a faster stabilization of the NH_2 high temperatures pathways, thus damping the instabilities and narrowing the oscillation window.



Figure 55. Reaction Rate analysis according to Zhang mechanism at ϕ =0.9, R=0.1, d=86%.

The analyses performed by the other kinetic mechanisms revealed consistent results about the role of hydrogen on ammonia oxidation mechanism. Indeed, whilst the LT oxidation pathways may change mechanism by mechanism, thus providing disagreement in the prediction of the species profiles and oscillations maps, it came out that H₂ promotes the NH₃ oxidation through the reaction NH₂+H₂=NH₃+H, as it is responsible of an increased concentration of H radicals. On the other hand, within the LT regime, the total H₂ conversion is partially delayed by NH₃ itself, that quickly consumes OH radicals, thus limiting the reaction H₂+OH=H+H₂O. The latter becomes relevant only for relatively high temperatures and controls the production of H radicals, replacing the role of the reaction NNH=N₂+H.

4.10.2. Analyses of the oxidation chemical kinetics of H₂/O₂/N₂-NH₃ system

The numerical simulations here reported aimed at understanding the kinetic pathways involved during the oxidations of the H_2/O_2 in presence of ammonia. Reaction Rates (RRs), flux diagrams and sensitivity analyses were realized for all the considered kinetic mechanisms. The reference case is the fuel-lean mixture (ϕ =0.5) diluted in Ar-NH₃(5%). Such a condition was chosen because it represents a compromise, since for lower ammonia concentration, H₂ chemistry still controls the oxidation process while, for higher ones, the occurrence of the "ammonia" saturation effect suggests the chemistry is controlled by ammonia. Anyway, simulations were run for lower and higher ammonia concentrations (herein not reported for the sake of briefness), that reinforce the numerical results elucidated in the next part of the thesis.

Apart of the different NH_3 oxidation pathways mechanism by mechanism, the overall description of the chemistry behind the delaying effect of NH_3 is the same according the analysed schemes. Therefore, for the sake of briefness and continuity, the results herein reported refer to the Zhang mechanism, without compromising the generality of the discussion.

First, the analyses of the oxidation of $H_2/O_2Ar-NH_3(5\%)$ mixture is presented through flux diagrams and sensitivity analyses at two different inlet temperatures, as to elucidate the main pathways and the change of the controlling reactions involved in the mixture oxidation chemistry with T_{in} . Following, a more detailed analysis is given through the Reaction Rates (RR analysis) as a function of T_{in} .

Figure 56 and Figure 57 show the flux diagrams and the sensitivity analyses at fixed T_{in} to describe the controlling reactions at T_{in} =920K and T_{in} =1100K temperatures. In each diagram, main species and radicals are reported in different colours (H₂=black, ammonia and nitrogen species=grey, main radical species=red). The same code colour is used for arrows to identify reactions where species are involved in. Arrow thickness is proportional to RR values (reported in the round brackets). The overall order of magnitude of the RRs is reported in the legend.

At $T_{in}=920K$ (Figure 56), H_2 is oxidized to H_2O by OH radicals (black arrows). NH_3 reacts with OH to produce NH_2 and H_2O . NH_2 is mainly reconverted back to NH_3 by reacting with H_2 according to the reaction $NH_2+H_2=NH_3+H$, justifying the low ammonia conversion. NH_2 reacts secondarily with HO_2 to produce H_2NO and HO_2 . H_2NO is again reconverted back to NH_2 , and secondarily to HNO and NO according to the reactions: $H_2NO+NH_2=HNO+NH_3$ and $HNO+O_2=NO+HO_2$.



Figure 56. Flux diagram and sensitivity analysis for a fuel-lean (ϕ =0.5) H₂-O₂ mixture diluted in Ar-NH₃(5%) at T_{in}=920 K.

branching mechanism is driven by HO₂ formation thought reaction The H+O₂+M=HO₂+M and consumption with NH₂ radicals. In fact, the reaction between NH₂ and HO₂ represents the main chain branching reaction as it is the principal source of OH radicals. It must be highlighted that both the reactions $NH_3+OH=NH_2+H_2O$ and $NH_2+H_2=NH_3+H$ are faster than $H_2+OH=H_2O+H$. This entails that NH_3 oxidation chemistry is more important than the H₂ one. The sensitivity analyses at T_{in} =920K suggest that, albeit the relevant role of the ammonia oxidation chemistry, H₂ chemistry controls the branching mechanisms trough the competition between H+O₂=OH+O and $H+O_2+M=HO_2+M$. The oxidation process has no sensitivity with respect to H_2O_2 formation $(HO_2+HO_2=H_2O_2+O_2)$ and decomposition $(H_2O_2+M=OH+OH+M)$, since preferentially reacts according HO₂ radical with NH_2 to the reaction $NH_2+HO_2=H_2NO+OH$. The reactions of NH_2 radicals back to NH_3 along with their recombination to N₂H₄ and oxidation with NO, exhibit a negative sensitivity coefficient to the temperature, while the reaction with HO₂ radicals a positive one, as it boosts the production of OH radicals.



Figure 57. Flux diagram and sensitivity for a fuel-lean (ϕ =0.5) H₂-O₂ mixture diluted in Ar-NH₃(5%) at T_{in}=1100 K.

Similar considerations apply to the flux diagram relative to $T_{in}=1100K$ (Figure 57). H₂ mainly react with OH radicals to produce H₂O and H, while NH₃ is mainly consumed by the oxidation pathway identified at lower temperatures (NH₂ \rightarrow H₂NO \rightarrow HNO \rightarrow NO). The oxidation of ammonia trough OH radicals is still prevalent on the oxidation of H₂ by the same radicals. It is worth noting that NH₂ recombination to N₂H₄ starts becoming important (NH₂+NH₂+M=N₂H₄+M, N₂H₄+NH₂=N₂H₃+NH₃, N₂H₃+H=N₂H₂+H₂). Once again, NH₂ radicals are reconverted back to NH₃ by H₂, while H₂NO and N₂H₄ to NH₂. For T_{in}=1100K, the branching mechanism is mainly controlled by H+O₂=OH+O. The sensitivity analysis at T_{in}=1100K (Figure 57) shows the branching mechanism is

controlled by the H₂ chemistry trough the competition between reactions $H+O_2+M=HO_2+M$ and $H+O_2=OH+O$. The reaction $NH_3+M=NH_2+H+M$ exhibits a negative sensitivity coefficient, since it consumes H radicals reconverting NH_2 to ammonia.

To further elucidate the interaction between the NH_3 and H_2 chemistry during oxidation, RRs analyses were performed as a function of T_{in} (Figure 58) in the range 800-1400K.

For low temperatures (Figure 58a), the oxidation of NH₃ by OH radicals is faster than $H_2+OH=H_2O+H$. The NH₂ radicals are converted back to ammonia reacting with H₂ (NH₃+H=NH₂+H₂) and with H radicals (NH₃+M=NH₂+H+M). To give at a glance the net rate of ammonia conversion, the sum of the rates of reactions NH₃+OH=NH₂+H₂O, NH₃+H=NH₂+H₂ and NH₃+M=NH₂+H+M is reported in the figure as "sum RRs" (dashed line). It is possible to note that the net reaction "sum RRs" is equal to the H₂ oxidation through OH radicals up to T_{in}=1150K, then it becomes slightly higher.

At low temperatures, even though the ammonia oxidation with OH radicals is very fast, NH₂ radicals are mainly converted back to ammonia through the reaction with H₂. In
addition, it is possible to note that reactions $H+O_2+M=HO_2+M$ and $NH_2+HO_2=H_2NO+OH$ control the branching mechanism.

At $T_{in}=1100K$, the reaction $NH_3+OH=NH_2+H_2O$ and $NH_3+H=NH_2+H_2$ reach respectively their maximum and minimum values, then $NH_3+OH=NH_2+H_2O$ decreases and at $T_{in}=1175K$ becomes slower that the reaction $H_2+OH=H_2O+H$. For the same inlet temperature, the reaction $NH_3+H=NH_2+H_2$ becomes positive, thus producing H_2 . The "sum RRs" is slightly lower than $H_2+OH=H_2O+H$, and NH_2 radicals are converted back to NH_3 only by reaction $NH_3+M=NH_2+H+M$.

For high temperatures, H_2 chemistry controls the system reactivity, through the branching mechanism sustained by reaction $H+O_2=OH+O$.

The RRs analysis confirms the controlling role of $H+O_2+M=HO_2+M$ on the oxidation process at low temperatures. The role of such reaction is emphasized in presence of strong colliders [48], thus suggesting that the inconsistency between numerical prediction and experimental data could be attributed to undeclared third body collisional efficiency for NH₃ in the kinetic mechanisms.



Figure 58. Reaction Rates analysis for a fuel-lean (ϕ =0.5) H₂-O₂ mixture diluted in Ar-NH₃(5%) for T_{in}=800-1400 K

On the basis of such considerations, further simulations were performed by declaring a third body efficiency for NH₃ in the reaction $H+O_2+M=HO_2+M$. The third body efficiency of NH₃ was changed from 10 to 30 with a step of 10. The results obtained by the modified Zhang mechanism are reported in Figure 59.



*Figure 59. Effect of declaring a NH*³ *third body efficiency in Zhang mechanism on the numerical profiles, for the mixture diluted in and Ar-NH*₃(5%).

In general, the system reactivity decreases as the NH₃ third body efficiency increases, with a higher sensitivity to the declaration of the third body efficiency (10 as much as water), while the percentage variation decreases with a further increase of the efficiencies. The temperature and species profiles show that the onset of reactivity occurs at higher T_{in} as NH₃ collisional efficiency increases. For instance, at T_{in}=1000K, Δ T passes from 16K to 9K and O₂ concentration increases from 2.0% to 2.5% if NH₃ collisional efficiency is increased from 1 to 30 in the kinetic mechanism. A further increase of the NH₃ third body collisional efficiency does not provide a better agreement between data and numerical profile.

The same attempt for the other mechanisms suggested similar results, confirming the models are sensitive to the declaration of such a parameter. A collisional efficiency higher than that assumed for water (equal to 10) was required to reproduce the experimental trend. In fact, the best fit of the experimental data is obtained by declaring a third body efficiency equal to 30, thus 3 times larger than the one declared for H₂O. To some extent, this result is congruent with the experiments that suggest NH₃ has an inhibiting effect on H₂ oxidation stronger than H₂O.

Summarizing the main outcomes from the kinetic analyses, it can be stated that under low-intermediate temperatures, the oxidation chemistry of NH₃ and H₂ is characterized by a mutual inhibiting interaction: NH₃ partially delays the H₂ conversion, because it acts as OH radicals scavenger through the reaction NH₃+OH=NH₂+H₂O. On the other hand, H₂ reconverts back NH₂ radicals to NH₃, through the reaction NH₂+H₂=NH₃+H. Because of H₂ conversion is limited by this interaction, H radicals, to sustain the typical hightemperature reaction of the H₂-O₂ system H+O₂=OH+O, comes only from the reaction NH₂+H₂=NH₃+H. In addition, the reaction H+O₂+M=HO₂+M becomes competitive with H+O₂=OH+O. The role of NH₃ as collider is not really contemplated in available kinetic mechanisms, but ammonia is likely to behave as a "strong" collider, given its physical/chemical properties. This aspect could cover a key-role to improve kinetic model performances for the investigated conditions.

The ammonia-hydrogen mutual inhibiting interaction disappears at high temperatures because NH₂ radicals are involved in faster kinetic pathways to NH (thus they are not reconverted back to NH₃). In turns, the H₂ and NH₃ oxidation chemistry decouples.

5. DISCUSSION

5.1. Uncertainty in modelling NH₃ oxidation and pyrolysis

As discussed in the Paragraph 2.1, the oxidation process of ammonia has been extensively studied for decades due to the importance of this molecule for the formation of NO_x from organically bound nitrogen in fuels and for NO_x reduction by the Thermal DeNO_x. Typical of such processes, the temperatures considered are relatively high and ammonia is present only in trace amounts. Therefore, under such conditions, the controlling kinetics are mainly related to the NH₃-NO interaction. Nonetheless, although extensively studied, the controlling reactions are currently affected by non-negligible uncertainties. Furthermore, with a view of using ammonia as a carbon-free fuel, knowledge of these processes is not sufficient to characterise the ammonia oxidation process. Indeed, operating conditions such as low temperatures, high reactants concentrations and high pressure promote completely different and more complex kinetic pathways than the ones involved in NH₃-NO interaction, which need to be carefully studied [136].

With reference to the experimental data and kinetic analyses reported in the Paragraph 4.1, ammonia oxidation pathways, as well as the formation of H₂ and NO, are strongly dependent on the reactions of the NH₂ radical, whose kinetics control the identified combustion regimes.

Specifically, it was showed that the models predicting increased reactivity base the lowtemperature oxidation on the recombination kinetics of the NH₂ radical to N₂H_x species, which are responsible for increased production of H₂ and H radicals. As a result, these mechanisms overestimate H₂ formation and reactants conversion, while underestimating NO concentration. The latter is strongly dependent on HO₂ radicals and DeNO_x kinetics. On the other hand, the mechanisms predicting lower reactivity suggest that the lowtemperature oxidation depends mainly on the formation of oxygenated intermediates, such as H₂NO and HNO, and on DeNO_x kinetics, leaving recombination reactions in the background. In this case, the system reactivity depends on the formation of HO₂ radicals while H₂ formation is almost negligible, as it is mainly related to the recombination reactions. Nevertheless, despite the greater importance of these kinetics, NO formation is not well described, as the pathways responsible for NO formation and reduction are not properly balanced and suffer from considerable uncertainty.

In general the non-monotonic trend of NO, reported in this thesis for several conditions, is not predicted by any of the considered kinetic mechanisms. This peculiar behaviour has to be related to a switch from formation to consumption (DeNO_x) pathways of NO, in agreement with references [62,130,137]. As showed from the Paragraph 4.1, first NO concertation increases up to a maximum relative value ($T_{in}=1150K$), then it decreases to a minimum value (approximately for $T_{in}=1250K$) independently on ϕ . Afterwards, NO emissions trend depends on ϕ . The non-monotonic trend is due to the activation of DeNO_x routes, as experimentally demonstrated in the Paragraph 4.5.

For low temperatures, the NO formation routes from ammonia, especially for fuel ultralean conditions are affected by large uncertainties [62,138]. This justifies the efforts made by many authors to properly model the NO formation for low-intermediate temperatures. In general, numerical predictions are sensitive to the reactions NH₂+NO=N₂+H₂O, NH₂+NO=NNH+OH and NH₂+HO₂=H₂NO+OH [62,116,119]. Recently, much attention has been devoted to the reaction H₂NO+O₂=HNO+HO₂ [116,139,140]. The reaction NH₂+HO₂=H₂NO+OH has been also recently revised by Klippenstein and Glarborg [141] through theoretical analyses, along with the reaction $NH_2+NO_2=N_2O+H_2O$ [142]. All considerations suggest that the whole NO formation these route $(NH_2 \rightarrow H_2NO \rightarrow HNO \rightarrow NO)$ needs to be properly addressed.

On the other hand, NH₂ recombination channel should be revised as well, as a concurrent route that inhibits NO formation pathway (NH₂ \rightarrow H₂NO \rightarrow HNO \rightarrow NO), while promoting H₂ production.

The importance of recombination reactions has been recently recognised by several authors [50,82,119,122,138,143].

Shrestha et al. [119] demonstrated that the exclusion of N_2H_x sub-mechanism from their kinetic model entails of lower laminar flame speed for all the investigated fuel-air equivalence ratios. Mathieu and Petersen [47] identified N_2H_x reaction set as the main difference between their kinetic scheme and the one of Klippenstein et al. [138]. In particular, the greater importance of N_2H_2 reactions in Klippenstein et al.'s mechanism promotes a faster ignition.

A recent work published by Marshall et al. [136] recognized the importance of the formation of N₂-amines, such as hydrazine (N₂H₄) and diazene (N₂H₂), in modelling the combustion of NH₃ and N₂H₄. In particular, they claimed that the chemistry of diazene, formed directly by amine–amine reactions or from sequential H-abstraction from N₂H₄, has been shown to be crucial for predicting flame speeds of ammonia and hydrazine, as well as for oxidation of NH₃ under flow reactor conditions. Therefore, they characterised the pressure and temperature dependence of key reactions involved in diazene formation and consumption through quantum chemistry methods and unimolecular rate. They emphasized the isomerisation between the E (trans) and Z (cis) forms of N₂H₂ and the relative importance of the diazene isomers. Moreover, they revised the addition of H atoms to form N₂H₃ and the abstraction by H atoms yielding NNH.

Despite all the recent efforts, NH₂ recombination to N_2H_x is described with kinetic rate constants largely different mechanism by mechanism. For instance, Figure 60 shows the Arrhenius plot for the reaction NH₂+NH₂=N₂H₂+H₂, based on the kinetic constants (k) declared for the schemes considered in this thesis. According to Nakamura and Konnov, k-value for N₂H₂ formation is 2 orders of magnitude greater than the one by Glarborg and Zhang and 4 order of magnitude greater than the one by Otomo.

Indeed, for Nakamura and Konnov mechanisms, such reaction has been identified as the one that increases the overall system reactivity through the steps $NH_3 \rightarrow NH_2 \rightarrow N_2H_2 \rightarrow NNH \rightarrow N_2+H$. As proof, the underestimation of this reaction compromises the system reactivity at low-intermediate temperatures, as for the Glarborg, Song, Zhang,

Otomo mechanisms, while the Nakamura and Konnov models predict higher reactivity because of the relatively higher k-values, considering the kinetic constants declared in these mechanisms.

In addition, it was also demonstrated that the $NH_2+NH_2=N_2H_2+H_2$ reaction is fundamental for the establishment of dynamic behaviours, due to the competition with the reactions $NH_2+OH=NH+H_2O$, as previously discussed. Indeed, Nakamura and Konnov mechanisms predict temperature oscillations for similar temperature window, while the other models predict instabilities for a narrower range of operative conditions.



Figure 60. Arrhenius plot for the reaction $NH_2+NH_2=N_2H_2+H_2$ according to different kinetic mechanisms.

The comparison between experimental and numerical results reported in Paragraph 4.5 highlighted, in line with Kobayashi et al. [66] suggestions, the lack of fundamental understanding also for ammonia pyrolysis, with severe implications on the oxidation routes. Indeed, even though the results here presented showed the interference of surface reactions, the onset of ammonia decomposition was found to occur about 1150K, independently of catalytic effects, and it is far to be predicted by all the considered schemes. Experimental evidences from Abian et al. and [144] Benés et al. [133] in flow reactors confirm such temperatures range as relevant for the beginning of NH₃ decomposition.

In general, ammonia pyrolysis is addressed through experimental data at high temperatures and with very low concentration of reactant [122,145]. Alturaifi et al. [54] recently developed a new kinetic model for NH₃ pyrolysis, based on shock tube experiments performed at near atmospheric pressure for a temperature range 2100-3000K, in two types of mixtures: ~0.5% NH₃ in Ar and ~ 0.42 NH₃/2% H₂ in Ar. Despite the model was tested against other experimental data of NH₃ pyrolysis available in literature, it is not able to capture the onset of reactivity of the experimental data here reported, suggesting that such discrepancy can be indicative of a missing pathway in current models. New pathways could be represented by the formation of larger N_yH_x

species (like N₃H₅ and N₂H₆), as discussed by Dana et al. [146] regarding the thermal decomposition of hydrazine or, merely, by new products channels for NH₂-NH₃-N₂H_x interaction. For instance, the reaction NH₃+NH₂=N₂H₃+H₂ was studied by Konnov and De Ruyck [122] for modeling the thermal decomposition of ammonia and it is not always included in recent kinetic models. Abian et al. [144] investigated the impact of the presence of such reaction to predict NH₃ pyrolysis and they demonstrated that, when it is not included in the mechanisms, the predicted onset of reactivity occurs at much higher temperatures than observed experimentally.

Another crucial aspect that needed to be assessed is the ammonia behavior as strong collider. The declaration of a collisional efficiency for NH₃ in kinetic mechanisms, and, in particular in H₂-O₂ sub-mechanism, can have strong implication in modeling NH₃ oxidation and speciation, especially in case of high NH₃ concentration. Actually, it can emphasize the role of H+O₂+M=HO₂+M, with direct implication on NO and H₂ profiles. Indeed, at low temperatures, the NO formation route is strongly dependent on the HO₂ concentration, that reacting with NH₂ forms H₂NO, subsequently converted into HNO and then NO (H₂NO→HNO→NO).

On the other hand, the competition between the reactions $H+O_2=OH+O$ and $H+O_2+M=HO_2+M$ is crucial to properly predict the H_2 profile in both NH₃ and NH₃-H₂ oxidation, as it determines the H_2 consumption and the composition of the radical pool.

As deductively demonstrated in the Paragraph 4.9, the NH₃ inhibiting effects on the H₂-O₂ chemistry seems to be even more drastic than H₂O, corroborating the possible role of ammonia as a third body species. This can be reasonably accepted considering the similar chemical nature of ammonia and water (as reported in Figure 3), since ammonia has a permanent dipole moment comparable to H₂O, a large cross section and, in addition, it is polarizable. Chemical kinetic theories recognize the importance of such chemical/physical properties, while they cannot clearly explicate such functionalities. These considerations highlight the need to reassess, in general, the role of polar molecules as a third-body species in combustion chemistry, with strong implications on the

development of detailed kinetic schemes.

5.2. Optimization of chemical kinetic mechanism

The discussion in the previous section highlighted the main critical issues in modelling ammonia oxidation under conditions relevant to unconventional combustion processes (MILD). Indeed, on the basis of the experimental data collected and by means of kinetic analyses, the reactions and kinetic pathways that may be responsible for discrepancies between models and experimental data have been suggested.

With this in mind, a final effort to model NH₃ oxidation features was made, supported by a collaboration with prof. Fabian Mauß and Dr. Krishna P. Shrestha from Brandenburg University of Technology, given their expertise in the modelling field.

The experimental data reported in the Paragraph 4.5 were selected as target to improve the prediction of the kinetic mechanism by Shrestha et al. [147], hereafter referred to as Shrestha2021. This mechanism is the improved version of their previous work [119] and it was validated for a wide range of conditions.

In this thesis, Shrestha2021 kinetic model was further improved to cover the current experimental data, updating it with more accurate rate constants reported recently in literature. The updated reactions are briefly described below.

The rate constants of the DeNO_x reactions NH₂+NO=NNH+OH (chain propagating) and NH₂+NO=N₂+H₂O (chain terminating) were updated, adopting from the shock tube experimental work of Song et al. [148]. They proposed rate constant in a temperature range of 200-2500 K. It was observed that adopting the rate from [148] remarkably improved the model predictions of NH₃/NO interaction. Moreover, these reactions were also found to be very sensitive to the predictions of pure ammonia oxidation.

Similarly, the reaction of NH_2+NO_2 has two paths H_2NO+NO and N_2O+H_2O . The reaction rates of these reactions were adopted from the theoretical work of Glarborg et al. [62].

The rate constant of H₂NO+O₂=HNO+HO₂ was implemented from the work of Cañas et al. [139]. Recently, they performed a theoretical high-level study to characterize the accurate rate constant of this reaction and proposed the rate constant in temperature range of 500-1700 K. Such reaction has been a subject of discussion due to its importance at low temperatures, as found in this thesis as well.

Stagni et al. [140] performed the experimental and theoretical study to characterize the combustion behavior of ammonia. They reported the rate constant of some reactions in HNO sub-mechanism which were calculated by *ab initio* method. In this work, the reaction rates of the following reactions were adopted from Stagni et al. [140]: HNO=H+NO, HNO+OH=NO+H₂O and HNO+NO₂=HNO₂+NO.

Chen et al. [149] performed a detailed investigation into the isomerization and decomposition of HONO and HNO₂ using state of the art electronic structure theory. They calculated the temperature and pressure dependent rate coefficients using microcanonical rate theory and the master equations. The proposed rate constants were adopted for the following reactions [149]: NO+OH=HONO, HNO+OH=HONO+H, HONO+H=NO₂+H₂, HONO+H=NO+H₂O, NO+OH=HNO₂, HNO₂+H=NO₂+H₂, HONO+H=HNO+OH, HNO+OH=HNO₂, HNO₂+H=NO₂+H₂, HNO₂+H=HNO+OH, HNO+OH=NO+H₂O.

Recently, the diazene chemistry was deeply investigated by Marshall et al. [136] using density function theory. They mainly focused on the reaction paths that create or consume this species (HNNH) and isomerization between the *trans* and *cis* forms. Therefore, they distinguished between the *cis* and *trans*-HNNH and reported the rate constants involving *cis* and *trans* form. In this thesis, both *cis* and *trans* HNNH species and reactions involving them were implemented, according to the work of Marshall et al. [136]. Here after, *trans* and *cis* form were implemented as N₂H₂ and cN₂H₂ respectively in the updated mechanism. The adopted reactions are: N₂H₂(+M)=cN₂H₂, N₂H₂(+M)=NNH+H, cN₂H₂ (+M)=NNH+H, N₂H₂+H=NNH+H₂, cN₂H₂+H=NNH+H₂, N₂H₃+H=N₂H₂+H₂, N₂H₃+H=cN₂H₂+H₂ and N₂H₃+H=H₂NN+H₂. Also the thermochemistry of N₂H₂ and cN₂H₂ and cN₂H₂ were implemented from Marshall et al. [136]. These reactions were found to be

very sensitive in the investigated conditions, since they significantly improved the model predictions.

The reaction NH₃+NH₂=N₂H₃+H₂ was found to be highly sensitive in this study as well, in particular for the formation of H₂ at low temperatures for both oxidative and pyrolytic conditions. Indeed, this reaction was responsible for the shift of the H₂ profile to lower temperatures and it also significantly affected NO profile. As discussed above, this reaction is not included in many of the recently published ammonia mechanisms and no extensively studies are available for it. One available rate constant for this NH₃+NH₂=N₂H₃+H₂ is from the experimental and modeling work of Dove and Nip [150] which dates back to 1979. They studied the ammonia pyrolysis in shock tube for temperatures in the range 2500-3000K and NH₃ concentration from 0.14% up to 6%, thus they obtained the rate constants for NH₃+NH₂=N₂H₃+H₂ via numerous iterations to match their experiment. Therefore, the rate constant from Dove and Nip [150] was here adopted and increased by factor 2 to have a reasonable agreement against experiments for a wide range of conditions.

Furthermore, in the current mechanism, NH_3 was declared as a third body species with a collisional efficiency equal to 12 in all the reactions involving the third body.

The complete list of updated reactions can be found in the Appendix.

The comparison between experimental data and model prediction is reported below.

In order to simplify the approach to the problem, simulations were performed under isothermal conditions, considering as reference temperature the reactor temperature at steady state (T=T_{in}+ Δ T). The simulations were performed using the LOGEresearch 1.10.0 software package [151].

Figure 61 reports the experimental results showed in Paragraph 4.5 (species profiles) for the oxidation of the NH₃/O₂ and NH₃-NO/O₂ mixtures, compared with model predictions for the current mechanisms (solid lines) and Shrestha2021 model (dashed lines), with the same color code. The results are plotted against the reactor temperature (T) at steady state conditions.



Figure 61. Experimental and numerical species profiles as a function of the temperature for NH_3 and NH_3 -NO mixtures oxidation, at ϕ =0.8, diluted in N_2 at 86%.

Consistently with the experimental data, numerical results show that O₂ consumption is not affected by the initial NO content, even though the current model predicts an overall

higher reactivity, while the previous version exhibits lower reactivity compared to the experimental data.

The non-monotonic trend of NO for the reference case is well captured by the current mechanism. Good results are obtained also for the prediction of NO profiles for the NH₃-NO mixtures, whereas the previous mechanism suggests the occurrence of NO reduction by NH₃ at temperature lower than the experimental evidences. The current mechanism even captures the H₂ trend, showing a good agreement with experiments for T>1300K. Despite the H₂ formation is shifted to higher temperatures, it can be noticed that significant improvements were achieved in modeling H₂ profile compared to the previous mechanism and other kinetic models (as reported in the previous paragraphs), due to the declaration of new reactions and kinetic parameters for the recombination of NH₂ to N₂H_x species and their subsequent decomposition. Indeed, such reactions are expected to be crucial in modelling the oxidation of NH₃ under low-temperature and low-dilution conditions [136], as discussed in details in the Paragraph 5.1.

The flux diagrams analyses reported in Figure 62 highlight the importance of the different NH₂ pathways for the different regimes (1070, 1250, 1350K). To directly compare the effect of NO addition to the reaction paths, additional dashed arrows are reported for the reactions that are more affected by NO, thus they are not showed when the effect is marginal.

In case of pure NH₃ oxidation at low temperatures, the diagrams show that the formation of H₂NO through the reaction NH₂+NO₂=H₂NO+NO is one of the favored paths for NH₂ consumption. NH₂ is also involved in the DeNO_x reactions (NH₂+NO=N₂+H₂O and NH₂+NO=NNH+OH). Specifically, at T=1070K, the terminating reaction NH₂+NO=N₂+H₂O is faster than the propagating one NH₂+NO=NNH+OH, resulting in a slow reactant conversion. The recombination pathway of NH_2 to N_2H_3 accounts for only 5% of NH₂ reactions. Nevertheless, the H₂ formation is very sensitive to the N₂H_x pathway, in particular the reaction NH₃+NH₂=N₂H₃+H₂ is responsible of the H₂ production at low-intermediate temperatures. The H₂ consumption through the typical H₂/O₂ oxidation chemistry is partially inhibited by NH₃ retarding effect as collider, since its third body efficiency enhances the role of the $H+O_2+M=HO_2+M$, delaying the high temperature branching mechanism (H+O₂=OH+O). In addition, due to the importance of such reaction, the HO₂ formation is promoted for low-intermediate temperatures, thus boosting also the NO production.

As the temperature increases (T=1250K), the relative balance of oxidative, recombination and DeNO_x pathways changes. Indeed, NH₂ is mainly involved in NH formation, that subsequently recombines with NH₂ to produce N₂H₂. The pathway NH \rightarrow N₂H₂ \rightarrow NNH \rightarrow N₂ promotes the formation of H₂ and H radicals, that enhances the system reactivity.



Figure 62. Flux diagrams analyses for NH₃ and NH₃-NO oxidation. Solid lines: main pathways for pure NH₃. Dashed lines: effect of NO addition on the main pathways.

Moreover, the reactions NH_2+NO become predominant compared to H_2NO formation *via* $NH_2+HO_2=H_2NO+OH$. As a consequence, NO formation pathway is slowed down in favor of the reduction one, resulting in the decreasing NO profile as a function of the temperature for T=1150-1250K.

For higher temperatures (T=1350K), the H_2/O_2 branching mechanism boosts OH formation, thus the high temperature reactivity is dominated by the conversion of NH₂ to NH, according to the reaction NH₂+OH=NH+H₂O, while the H₂NO formation and the DeNO_x reactions cover a secondary role. Therefore NH is mainly consumed through the recombination pathway to N₂H₂. In addition, the NH paths also contribute to NO formation, along with the H₂NO/HNO reactions, since NH reacts with O₂ and OH radicals to directly produce NO. Despite the increased reaction rate of the NO reduction, such new pathways to NO formation led to increase the NO concentration as a function of the temperature.

The major impact of NO addition to NH_3 oxidation pathways is observed for low and intermediate temperatures. At T=1080K, the terminating DeNO_x reaction $NH_2+NO=N_2+H_2O$ prevails over the chain propagating one ($NH_2+NO=NNH+OH$) and the H₂NO formation, resulting in a slight decrease of NO concentration, without significant effect on the overall system reactivity, as observed from the experimental results. As the temperature increases (T=1250K), the reaction $NH_2+NO=NNH+OH$ becomes faster than the terminating one, enhancing the formation of both OH and H radicals, the latter mainly formed by NNH decomposition.

An important aspect that needs to be stressed is the high impact of the declaration of a collisional efficiency for NH_3 and other nitrogen-species. Since the reaction $H+O_2+M=HO_2+M$ controls the formation of HO_2 radicals at low temperature, the prediction of the system reactivity and species profiles (in particular, NO concentration) worsens considerably when such parameter is not included in the kinetic mechanism.

The relatively high value declared for ammonia (equal to 12) compared to other species is in line with the experimental evidences reported in the Paragraph 4.9. Indeed, the current model well reproduce the effect of NH₃ on H₂-O₂ oxidation.

It is also important to emphasize that the declaration of new reactions and kinetic parameters for the recombination of NH_2 to N_2H_x species and their subsequent decomposition, as well as the inclusion of the reaction $NH_3+NH_2=N_2H_3+H_2$, noticeably improved the prediction of H_2 in the low temperature regime, corroborating the necessity to properly address ammonia decomposition to describe also its oxidation.

Due to the new set of reactions, also the prediction of NH₃ pyrolysis changed drastically, as reported in Figure 63.



Figure 63. Experimental and numerical H_2 for NH_3 pyrolysis diluted in Ar at 92%.

Although far from correctly predicting the experimental data, the current model shows the onset of reactivity at significantly lower temperatures than Shrestha2021 model and the other considered mechanisms.

5.2.1. Validation against literature data

The performance of the current mechanism was further evaluated against different literature data for NH₃-NO interaction and NH₃ oxidation. In particular, the performances of the mechanism were verified for experimental data on NH₃-NO interaction from Dagaut [131] and Alzueta et al. [130] and for NH₃ laminar flame speed [119] and ignition delay time [47] at different equivalence ratios.

Figure 64 shows the results for NH₃-NO oxidation in JSFR for various equivalence ratios (0.1, 2) and initial concentrations of NO equal to 500 and 1000 ppm, at atmospheric pressure [131]. The experiments were performed as a function of the temperature in the

range 1100-1450K, at fixed residence time (0.1s). The prediction of Shrestha2021 mechanism is reported as dashed line on the same plot. The present model well reproduces the NH₃, H₂O and NO profiles at fuel lean conditions, for different initial concentrations of NO. The mixture reactivity at fuel-rich conditions is not reproduced by the mechanism, that predicts a lower reactivity compared to the experimental data.



Figure 64. Speciation of NH₃/NO oxidation in a JSFR at atmospheric pressure for different air excess ratio. Symbols: experimental data from Dagaut [131]. Solid lines: prediction with the present mechanism. Dashed lines: prediction with Shrestha2021 mechanism.

The NH₃-NO interaction was experimentally investigated recently by Alzueta et al. [130] in a laboratory tubular flow reactor at atmospheric pressure, for temperatures in the 700-1500K range, various air excess ratio (λ) and NH₃/NO ratio in the range 0.7-3.5. The NH₃ and NO profiles in comparison to model predictions are reported in Figure 65. The prediction of Shrestha2021 mechanism is reported as dashed line on the same plot.



Figure 65. Speciation of NH₃/NO oxidation in a flow reactor at atmospheric pressure for different air excess ratio. Symbols: experimental data from Alzueta et al. [130]. Solid lines: prediction with the present mechanism. Dashed lines: prediction with Shrestha2021 mechanism.

The present mechanism well reproduces NH₃ and NO profiles at λ =1.65, 1.01. For fuelrich condition (λ =0.55), the model underestimates the system reactivity, as it predicts reactants conversion for T>1350K, while the experiments show that NH₃ and NO decrease for T>1250K.

Figure 66 reports the predicted NH₃/air laminar burning velocities in comparison to experimental data collected by Shrestha et al. [119]. The measured burning velocities exhibit a good agreement for fuel-lean and stoichiometric conditions, while discrepancies can be noticed for the rich conditions.

The model is able to predict the experimental data from fuel-lean to stoichiometric conditions, showing the best agreement with data by Pfahl2000. For fuel-rich conditions (ϕ <1.4), the mechanism prediction is in good agreement with the experiments by Ronney1988, but it predicts higher flame speed for ϕ >1.4.



Figure 66. Laminar flame speed for NH₃/air mixtures at 298K and 1atm. Symbols: experiments adapted from by Shrestha et al. [119]. Solid lines: prediction with the present mechanism. Dashed lines: prediction with Shrestha2021 mechanism.

The mechanism predictions for NH₃/O₂ ignition delay time from shock tube experiments are showed in Figure 67. The experiments were reported by Mathieu and Petersen [47], for mixtures diluted in Ar at 98% and 99%, for various pressures (1.4, 11, 30 atm) and equivalence ratios (0.5, 1.0, 2.0).

The present model well reproduces the ignition delay time for fuel-lean and stoichiometric conditions, with small discrepancies for the data at 30 atm diluted at 98% in Ar. For the fuel-rich mixture, the mechanism is able to predict the experimental data for high pressure conditions, whereas it shows lower reactivity compared to the experiments at atmospheric pressure.



Figure 67. Ignition delay time data from shock tube experiments for NH₃/O₂/Ar mixtures, at various pressures (1.4, 11, 30 atm) and equivalence ratios (0.5, 1.0, 2.0). Solid lines: prediction with the present mechanism. Dashed lines: prediction with Shrestha2021 mechanism.

6. CONCLUSIONS

The present thesis provided a detailed experimental and numerical characterization of the oxidation process of diluted and pre-heated ammonia and ammonia-hydrogen mixtures, at nearly atmospheric pressure, in a Jet Stirred Flow Reactor, covering a wide range of operating conditions, in terms of temperature, mixture composition, diluent species and dilution level. The influence of these parameters on stable species concentration profiles and combustion regimes was analyzed, providing new insights into ammonia oxidation process, as well as significant targets and constraints for the validation of detailed kinetic mechanisms, in particular for non-conventional operating conditions. In addition, the analyses of low-intermediate temperature conditions provided relevant information for ammonia applications in engines and gas turbines.

Several main finding can be outlined by the results here presented, as summarized below:

- 1) Identification of oxidation regimes. The main species profiles suggested the existence of three different kinetic regimes for the ammonia oxidation depending on the system inlet temperatures (T_{in}). They were classified as low (T_{in} <1100 K), intermediate (1100< T_{in} <1250 K) and high temperatures (T_{in} >1250 K). The low-intermediate temperature regimes (which will be referred below as Low-Temperature LT regime for simplicity) are characterized by a low ammonia conversion. In the LT regime, the reference species trends are very similar for the considered equivalence ratio, thus the reactivity of the mixtures is almost independent of the mixture composition. For temperatures higher than 1225 K (High Temperature regime, HT) a strong ignition occurs and ammonia is completely converted. In this case, the NO and H₂ concentrations show a strong dependence on the equivalence ratio with species distribution trends significantly different.
- 2) Identification of instabilities. Experimental analyses preformed following the evolution of the reactor temperature (T_r) in time allowed to identify transient and dynamic behaviors. In particular, it was found that the shift from the LT to HT occurs at a noticeable reactor temperature (T_r =1300 K) independently of the mixture equivalence ratio, while the transitional mode may occur directly or through a Lower Reactivity (LR) regime (for 1300< T_r <1310K), with a slight decrease of overall system reactivity. The LR behavior was identified for fuellean up to the stoichiometric condition, while fuel ultra-lean and rich mixtures do not exhibit any change of reactivity. In addition, the transition between LR and HT behavior can occur through instabilities with the establishment of damped temperature for instabilities occurs for T_r =1320K. Also periodic oscillations were identified. The range of conditions for periodic instabilities is restricted to small temperature and ϕ windows, namely T_{in} =1255-1260K and ϕ =0.55-0.58. The

detection of such phenomenologies is only possible by adopting very tight $\Delta \phi$ and ΔT steps. This is explicable on the basis of the consideration that the experimental conditions where periodic oscillations establish are very limited with respect to the matrix of the JSFR control parameters. To some extent, the ammonia chemistry behaves as an on-off system, thus the transition through the LT and HT regime is not easy to detect.

3) Inconsistency in description of Low-Temperature oxidation. Numerical analyses were performed in order to understand the chemistry of the ammonia oxidation process by means of detailed kinetic models. Results showed that ammonia oxidation strongly depends on different NH₂ consumption routes promoted in diverse temperature ranges. The description of the LT reactivity is mechanism dependent and also the prediction of the main species profiles changes scheme by scheme. Some of the analyzed mechanisms suggest that NH₃ oxidation occurs through the formation of N₂H_x species according to the sequence $NH_3 \rightarrow NH_2 \rightarrow N_2H_x \rightarrow NNH \rightarrow N_2+H$. Others described the NH₃ oxidation through the formation of oxygenated intermediate species $(NH_3 \rightarrow NH_2 \rightarrow H_2NO \rightarrow HNO \rightarrow NO)$. Specifically, the models that predict increased reactivity base the low-temperature oxidation on the recombination kinetics of the NH₂ radical to N₂H_x, which are responsible for increased production of H₂ and H-radicals. As a result, they overestimate H₂ formation and reactants conversion, while underestimating NO formation. The latter is strongly dependent on HO₂ radicals and DeNO_x kinetics. In addition, for these mechanisms, the reaction rate analysis suggests that dynamic behaviors derive from a strong competition between NH₂ oxidation and recombination routes. On the other hand, the mechanisms predicting lower reactivity suggested that the lowtemperature oxidation depends mainly on the formation of oxygenated intermediates, such as H_2NO and HNO, and on $DeNO_x$ kinetics, while the recombination kinetics play a marginal role. In this case, the system reactivity depends on the formation of HO₂ radicals and H₂ formation is almost negligible, as it is dependent only on the recombination reactions.

At high temperatures, the overall description of NH_3 oxidation chemistry is congruent among all the mechanisms, thus key species and reaction pathways are the same. As further consequence of the different description of the ammonia LT chemistry, all the considered kinetic schemes failed to predict dynamic regimes, that mark the shift from LT to HT regimes.

4) Study on ammonia pyrolysis. In order to investigate the role of recombination and decomposition reactions, further experimental tests were performed on NH₃ thermal decomposition. Even though the results showed the interference of surface reactions, the onset of ammonia decomposition was found at about 1150K, independently of catalytic effects. The comparison between experimental and numerical results highlighted the lack of fundamental understanding also for ammonia pyrolysis, with great implications on the prediction of its oxidation features.

- 5) Study on ammonia-NO interaction. Experimental tests on NH₃-NO mixtures oxidation aimed at identifying the role of DeNO_x reactions on ammonia combustion chemistry. The NO profile for the oxidation of pure NH₃ showed a peculiar non-monotonic trend at low temperatures, independently of the mixture composition and diluent species. In particular, it exhibited a decreasing trend for temperature in the range 1150-1250K. For mixtures doped with NO, the concentration of NO remains equal to the initial value for T<1000K, while an abrupt NO concentration decrease occurs for T close to 1100K, independently of NO initial concentration. For T=1150-1250K, regardless of the initial NO concentration in the mixture, NO profiles almost overlap, suggesting the occurrence of fast DeNO_x reactions (NH₂+NO=NNH+OH and $NH_2+NO=N_2+H_2O$) and their relevant role in controlling NH_3 oxidation regimes.
- 6) Effect of hydrogen on ammonia instabilities. The effect of hydrogen on ammonia oxidation has been investigated by changing the H₂ content in inlet mixture, for different equivalence ratios and dilution levels, in a wide range of inlet temperatures. Experimental results showed that H₂ slightly enhances the reactivity of the system for low-intermediate temperatures and shifts the threshold T_r that marks the transition through the LR and DR to lower temperatures. The dynamic regimes have been fully investigated up to outline maps of instabilities in the T_{in} - ϕ plane. Increasing the H₂ content in the inlet mixture, the dynamic regimes areas shift towards lower T_{in} and extend in a narrower ϕ range. Nonetheless, even though NH₃ oxidation is slightly enhanced by hydrogen addition, the experimental results also revealed that the potential promoting role of H₂ is limited by NH₃ itself, that delays hydrogen conversion.
- 7) Mutual inhibiting interaction of ammonia-hydrogen. In order to address the inhibiting role of ammonia on hydrogen oxidation, further experimental tests were carried out for H₂/O₂/Ar and H₂/O₂/N₂ mixtures as reference cases under MILD operative conditions, then the oxidation process was analyzed replacing Ar or N_2 with variable amounts of ammonia, parametrically changing the ammonia concentration. Results are then compared with experimental evidences for mixtures partially diluted in water. Experimental tests suggest that ammonia strongly interacts with the H₂ oxidation chemistry within the considered operative conditions, with an overall delaying effect on H₂ characteristic chemical times. As a direct evidence, the onset of the system reactivity is shifted towards higher inlet temperatures as the ammonia concentration increases. In addition, hydrogen instabilities, identified for the mixtures $H_2/O_2/Ar$ and $H_2/O_2/N_2$, disappear as soon as ammonia is added to reactants. In particular, the experimental evidences suggest that a concentration of NH₃ of 10% is able to retard the onset of the reactivity of the $H_2/O_2/Ar$ and $H_2/O_2/N_2$ of about 50-75K, relatively to the operative conditions considered. A further increase of ammonia concentration

does not seem to alter the overall system reactivity, showing that the mixtures reactivity is very sensitive to ammonia even if in small concentrations, while increasing ammonia content the reactivity goes towards a "saturation" effect, with a lower variation on mixtures reactivity with an increase of ammonia concentration. At the same time, despite the different heat capacities of the mixtures H₂/O₂/Ar and H₂/O₂/N₂, the reactivity of the mixtures is very similar when ammonia is added to the system, suggesting that mixtures thermal properties have a negligible impact on the ammonia delaying effect on H_2 oxidation chemistry. A similar delaying effect was identified also in the cases of mixtures partially diluted in water. As global effect, ammonia has resulted to be more effective than water to retard the H₂ characteristic chemical times. The delaying effect of water on H₂ oxidation was identified in its "strong" collider nature in the reaction $H+O_2+M=HO_2+M$, thus enhancing its reaction rate to detriment of the reactions H+HO₂=OH+OH and H+O₂=OH+O as OH radical sources. This, in turns, explains also the suppression of system instabilities. These considerations contribute to conceive a plausible role of ammonia as a "strong" collider in thirdbody molecular reactions. This hypothesis is also supported by the physical/chemical properties of ammonia, because it has a high polarity and a dipole moment comparable to water. As matter of fact, the "strong" collider nature of water in the reaction $H+O_2+M=HO_2+M$ is commonly attributed to the very strong polar-polar interaction with HO₂ radicals.

8) Ammonia as strong collider in third-body reactions. The kinetic analyses highlighted that, despite the different description of the LT ammonia oxidation pathways, models suggest consistent results about hydrogen-ammonia interaction. Under low-intermediate temperatures, the oxidation chemistry of NH₃ and H₂ is characterized by a mutual inhibiting interaction: NH₃ partially delays the H₂ conversion, because it acts as OH radicals scavenger through the reaction NH₃+OH=NH₂+H₂O. On the other hand, H₂ reconverts back NH₂ radicals to NH₃, through the reaction $NH_2+H_2=NH_3+H$. Because of H_2 conversion is limited by this interaction, H radicals, to sustain the typical high-temperature reaction of the H2-O2 system H+O2=OH+O, comes only from the reaction NH2+H2=NH3+H, whereas the role of direct H_2 oxidation is marginal. In addition, the reaction H+O₂+M=HO₂+M becomes competitive with H+O₂=OH+O and its role could be emphasized by the declaration of a third-body collisional efficiency for ammonia. The ammonia-hydrogen mutual inhibiting interaction disappears at high temperatures because NH₂ radicals are involved in faster kinetic pathways to NH (thus they are not reconverted back to NH₃). In turns, the H₂ and NH₃ oxidation chemistry decouples.

The role of NH_3 as collider is not really contemplated in available kinetic mechanisms, but ammonia is likely to behave as a "strong" collider, given its physical/chemical properties. This aspect could cover a key-role to improve kinetic model performances for the investigated conditions. As a further

implication, the evaluation of a plausible role of ammonia as a third body species may have intrinsic implications also for the other polar molecules (as fuels, energy carriers, or intermediate species, i.e. CO, formaldehyde, alcohols/bio-alcohols) in combustion chemistry as third-body species, given their physical/chemical properties (polarity and dipole moment).

- 9) Critical reaction pathways. The key reactions that were identified in this thesis must be considered for a further tuning of kinetic schemes, which is needed to proper describe ammonia and ammonia-hydrogen oxidation processes under low-temperatures operative conditions. The NO formation paths from ammonia, especially for fuel ultra-lean conditions, are affected by large uncertainties, in particular for low-temperatures. This justifies the efforts by many authors to properly model the NO formation routes for low-intermediate temperatures. NH₂ recombination channel should be revised as well. Indeed, despite all the recent efforts, NH₂ recombination to N₂H_x is described with kinetic rate constants largely different mechanism by mechanism. Finally, ammonia behavior as collider needs to be assessed. The declaration of a collisional efficiency for NH₃ in kinetic mechanisms, in particular in H₂-O₂ sub-mechanism, can have strong implication in modeling NH₃ oxidation and speciation, especially in case of high NH₃ concentration.
- 10) Kinetic mechanism optimization. On the basis of the experimental data collected and analysed by means of kinetic analyses, a final effort to model NH₃ oxidation was made, improving the performance of an existing detailed kinetic mechanism through the implementation of new reactions and the tuning the kinetic parameters of the most sensitive ones. The NH₃-NO experimental data was selected as target for modelling. The updated model successfully reproduced the target data and other literature data for NH₃-NO oxidation in flow reactors. Model advancements in the prediction of the non-monotonic NO profiles are ascribable to updated rate constants of NO formation reactions and $DeNO_x$ ones. The proper prediction of H₂ concentration relies on the declaration of new reaction parameters relative to NH_2 recombination to N_2H_x species and their relative decomposition. Significantly, also the role of ammonia as a strong collider has been included, declaring a collisional efficiency in all third-body reactions. The relatively high value declared for ammonia (equal to 12) compared to other species is in line with the experimental evidences reported in the thesis. Indeed, the current model well reproduce the delaying effect of NH₃ on H₂-O₂ oxidation.

In conclusion, the experimental results achieved in this thesis show novel fundamental aspects of ammonia combustion, thus representing an important contribution towards ammonia oxidation/pyrolysis understanding.

The study has been developed in a hierarchical way, passing from fundamental aspects of NH₃/O₂ mixtures to NH₃-NO/O₂ and NH₃-H₂/O₂ mixtures, in parallel with ammonia pyrolysis studies. Each step has been complemented by numerical simulations and kinetic analyses. This two-fold approach has suggested the

inconsistences of available kinetic mechanisms in predicting peculiar features of ammonia oxidation, highlighting the necessity to properly model $DeNO_x$ chemistry, introduce new sets of reactions (related to N_2H_x species), while recognizing the role of ammonia as a "strong" collider in third-body reactions.

In this context, although the considerable progresses here achieved, there is still room for improvement given the large uncertainties of N_2H_x species reactions, along with the ones related to NH₃ chaperon efficiencies in third-body reactions. Herein, it is worth mentioning this aspect should be extended also to N_2H_x species. In fact, the recognition of the role of ammonia as a collider in third-body molecular reactions, in virtue of its chemical/physical properties, paves the way for the introduction of thirdbody efficiencies for fuels and intermediate species characterised by considerable cross-sections or that may exhibit polar and/or polarisable behaviour.

Given this background, further studies are required, especially to properly model ammonia oxidation under fuel-rich conditions and ammonia pyrolysis.

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APPENDIX

List of changed	reactions with re	espect to Shre	estha2021 me	chanism. Rea	ction rates	are
given in the Ar	rhenius expressio	on as k=A T ⁿ	$exp[-E_a/RT]$.	Units are cal,	mol, cm, s	s, K.

No.	Reaction	Α	n	Ea	Comments
	NH ₃ sub-mechanism				
R1	$NH_{2}+H(+M)=NH_{3}(+M)$	1.60E+14	0	0.00E+00	
	Low-pressure limit	3.60E+22	-1.76	0.000E+00	
	L		1.00E-		
	Troe parameters	0.5	30	1.00E+30	
R2	$NH_3+H=H_2+NH_2$	6.67E+06	2.13195	1.09E+04	
R3	NH ₃ +O=NH ₂ +OH	4.43E+02	3.18	6.74E+03	
R4	NH ₃ +OH=NH ₂ +H ₂ O	4.30E+03	2.83021	-4.31E+02	
R5	NH3+HO2=NH2+H2O2	1.17E+00	3.839	1.73E+04	
R6	NH ₃ +O ₂ =NH ₂ +HO ₂	7.00E+09	1.285	5.52E+04	
R7	$NH_3+NH_2=N_2H_3+H_2$	1.90E+11	0.5	2.16E+04	
	NH ₂ sub-mechanism				
R8	NH2+O=HNO+H	3.30E+14	-0.5	0.00E+00	
R9	NH ₂ +O=NO+H ₂	5.00E+12	0	0.00E+00	removed
R10	NH2+OH=NH+H2O	6.04E+04	2.52	-6.16E+02	
R11	NH2+HO2=H2NO+OH	6.25E+17	-1.28	1.17E+03	
R12	NH2+HO2=HNO+H2O	1.60E+07	0.55	5.25E+02	
	DUPLICATE				
R12	NH2+HO2=HNO+H2O	5.70E+15	-1.12	7.07E+02	
	DUPLICATE				
R13	NH2+HO2=HON+H2O	2.10E+07	0.64	8.11E+02	
R14	NH2+O2=H2NO+O	2.60E+11	0.4872	2.91E+04	
R15	NH2+O2=HNO+OH	2.90E-02	3.764	1.82E+04	
R16	NH2+NH2=NH3+NH	1.35E+01	3.53	5.53E+02	
R17	NH2+NH=NH3+N	1.20E+04	2.46	1.07E+02	
R18	NH2+NO=N2+H2O	2.60E+19	-2.369	8.70E+02	
R19	NH2+NO=NNH+OH	4.30E+10	0.294	-8.66E+02	
R20	NH2+NO2=N2O+H2O	2.20E+11	0.11	-1.19E+03	
R21	NH2+NO2=H2NO+NO	2.15E+12	0.11	-1.19E+03	
R22	NH2+HNO=NH3+NO	1.62E+03	2.95	-3.47E+03	
R23	NH2+HONO=NH3+NO2	7.11E+01	3	-4.94E+03	removed
	NH sub-mechanism				
R24	N+NO=N2+O	9.40E+12	0.14	0.00E+00	
		2.00E + 12	0.11	0.00E + 00	
R25	NH+()H=HN()+H			$(f, (h, h)) \rightarrow (h, h)$	
R25 R26	NH+OH=HNO+H NH+OH=NO+H2	2.00E+13 1.20E+13	0	0.00E+00	

R28	NH+O ₂ =HNO+O	4.05E+11	0.09	1.07E+04	
R29	NH+O ₂ =NO+OH	2.01E+15	-1.38	5.67E+03	
R30	NH+NH=>N2+H+H	5.63E+13	-0.036	-1.61E+02	
R31	$NH+NH=>N_2+H_2$	6.26E+12	-0.036	-1.61E+02	
R32	NH+NO=N ₂ O+H	2.70E+15	-0.78	2.00E+01	
R33	NH+NO=N2+OH	6.80E+14	-0.78	2.00E+01	
	NNH sub-mechanism				
R34	NNH=N2+H	1.00E+09	0	0.00E+00	
R35	NNH+O=N ₂ O+H	1.90E+14	-0.274	-2.20E+01	
R36	NNH+O=NH+NO	5.20E+11	0.381	-4.09E+02	
R37	NNH+O ₂ =N ₂ +HO ₂	5.60E+14	-0.385	-1.30E+01	
R38	NNH+HO ₂ =N ₂ +H ₂ O ₂	1.40E+05	2.69	-1.60E+03	
R39	NNH+NO2=N2+HONO	1.74E+01	2.84	1.67E+03	
	N ₂ H ₂ sub-mechanism				
R40	$N_2H_2(+M)=cN_2H_2(+M)$	4.90E+09	1.18	4.77E+04	
	Low-pressure limit	3.00E+28	-3.56	5.61E+04	
	Troe parameters	0.35	650	1.06E+04	
	DUPLICATE				
R41	$N_2H_2(+M)=cN_2H_2(+M)$	1.50E+14	0	5.50E+04	
	Low-pressure limit	2.30E+29	-4	6.01E+04	
	Troe parameters	0.35	650	1.06E+04	
	DUPLICATE				
R42	$cN_2H_2+H=N_2H_2+H$	7.80E+08	1.58	2.18E+03	
R43	$N_2H_2+M=NNH+H+M$	1.90E+27	-3.05	6.61E+04	removed
R44	$N_2H_2(+M)=NNH+H(+M)$	6.30E+16	0	6.40E+04	
	Low-pressure limit	8.70E+39	-6.91	7.04E+04	
	Troe parameters	0.44	520	6.15E+03	
R45	$cN_2H_2(+M)=NNH+H(+M)$	2.20E+16	0	5.87E+04	
	Low-pressure limit	3.70E+35	-5.44	6.39E+04	
	Troe parameters	0.44	520	6.15E+03	
R46	$N_2H_2+H=NNH+H_2$	4.50E+07	1.8	9.00E+02	
R47	$cN_2H_2+H=NNH+H_2$	1.40E+08	1.72	4.70E+02	
R48	N ₂ H ₂ +O=NNH+OH	1.11E+08	1.62	8.05E+02	
R49	N ₂ H ₂ +NH ₂ =NNH+NH ₃	2.70E+05	2.226	-1.03E+03	
R50	NH ₂ +NH=N ₂ H ₂ +H	1.65E+14	-0.272	-7.80E+01	
R51	NH ₂ +NH=cN ₂ H ₂ +H	5.00E+13	-0.272	-7.80E+01	
R52	$NH_2+NH_2=N_2H_2+H_2$	3.40E + 08	1.02	5.93E+03	
R53	$N_2H_2+HO_2=NNH+H_2O_2$	5.00E+12	0	1.99E+03	
R54	$N_2H_2+M=NH+NH+M$	3.16E+16	0	9.94E+04	removed
R55	$NH+NH=N_2H_2$	7.83E+13	-0.036	-1.61E+02	
R56	N ₂ H ₂ +NO ₂ =NNH+HONO	1.12E-03	4.47	7.19E+03	
	N2H3 sub-mechanism				
R57	$N_2H_2(\pm M) - N_2H_2 \pm H(\pm M)$	1 30F±11	0 8 1 0	4 81F⊥04	
NJ/	Low-pressure limit	3.80E+40	-6 88	012+04 5.45E+04	
			0.00	U U L . U T	

D59	Troe parameters	80000	28	7.30E+03	
КЗО	N ₂ H ₃ +H=NH ₂ +NH ₂	1.00E+14	0	1.50E+03	
R59	$N_2H_3+H=N_2H_2+H_2$	4.60E+01	3.53	3.75E+03	
R60	$N_2H_3+H=cN_2H_2+H_2$	2.70E+02	3.18	6.62E+03	
R61	$N_2H_3+NH_2=N_2H_2+NH_3$	6.10E-01	3.574	1.19E+03	
R62	N2H3+NH2=H2NN+NH3	1.10E+01	3.08	2.11E+02	
R63	$N_2H_3+H=H_2NN+H_2$	3.10E+06	2.11	2.88E+02	
R64	$N_2H_3+M=NH_2+NH+M$	5.00E+16	0	6.00E+04	
	N2H4 sub-mechanism				
R65	$N_2H4=H_2NN+H_2$	1.40E+14	0	7.49E+04	
R66	N2H4+H=NH3+NH2	4.46E+09	0	3.10E+03	
R67	N ₂ H4+OH=N ₂ H ₃ +H ₂ O	2.35E+13	0	0.00E+00	
R68	$N_2H4+NH_2=N_2H_3+NH_3$	7.60E-01	4	4.05E+03	
R69	N ₂ H4+NO=N ₂ H ₃ +HNO	6.00E+01	3.16	3.08E+04	
R70	N ₂ H4+NO ₂ =N ₂ H ₃ +HONO	8.20E+01	3.13	8.86E+03	
R71	$N_2H4+NO_2=N_2H_3+HNO_2$	2.40E-02	4.14	7.95E+03	
	H ₂ NO sub-mechanism				
R71	H2NO+M=HNO+H+M	2.80E+24	-2.83	6 49E+04	
R72	$H_2NO+H=HNO+H_2$	1.00E+07	2	2.00E+03	
R73	$H_2NO+H=NH_2+OH$	8.50E+13	0	0.00E+00	
R74	$H_2NO+OH=HNO+H_2O$	3.00E+13	0	0.00E+00	
R75	H ₂ NO+NO ₂ =HONO+HNO	9.00E+11	0	2.00E+03	
R76	H2NO+NH2=HNO+NH3	3.60E+06	1.94	-5.80E+02	
	HNO sub-mechanism				
R77	HNO sub-mechanism	1 52F+15	-0.41	0.00F+00	removed
R77 R78	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO	1.52E+15 1.83E+20	-0.41	0.00E+00 4 79F+04	removed
R77 R78	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm	1.52E+15 1.83E+20 2.01E+19	-0.41 -3.008 -3.021	0.00E+00 4.79E+04 4.78E+04	removed
R77 R78	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20	-0.41 -3.008 -3.021 -3.008	0.00E+00 4.79E+04 4.78E+04 4.79E+04	removed
R77 R78	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21	-0.41 -3.008 -3.021 -3.008 -2.959	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04	removed
R77 R78	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21	-0.41 -3.008 -3.021 -3.008 -2.959 -2.855	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04	removed
R77 R78	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 1000 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21	-0.41 -3.008 -3.021 -3.008 -2.959 -2.855 -2.642	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04	removed
R77 R78	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 1000 atm HNO+H=NO+H ₂	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10	-0.41 -3.008 -3.021 -3.008 -2.959 -2.855 -2.642 0.94	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.95E+02	removed
R77 R78 R79 R80	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 1000 atm HNO+H=NO+H ₂ HNO+OH=NO+H ₂ O	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10	-0.41 -3.008 -3.021 -3.008 -2.959 -2.855 -2.642 0.94 0.39	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.95E+02 3.78E+03	removed
R77 R78 R79 R80	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 1000 atm HNO+H=NO+H ₂ HNO+OH=NO+H ₂ O 0 01 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10	-0.41 -3.008 -3.021 -3.008 -2.959 -2.855 -2.642 0.94 0.39 0.4	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.95E+02 3.78E+03 3.76E+03	removed
R77 R78 R79 R80	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 100 atm 1000 atm HNO+H=NO+H ₂ HNO+OH=NO+H ₂ O 0.01 atm 0 1 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.85E+10	-0.41 -3.008 -3.021 -3.008 -2.959 -2.855 -2.642 0.94 0.39 0.4 0.4	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.85E+04 4.89E+04 4.95E+02 3.78E+03 3.76E+03 3.76E+03	removed
R77 R78 R79 R80	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 100 atm $HNO+H=NO+H_2$ $HNO+OH=NO+H_2O$ 0.01 atm 0.1 atm 0.316 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.85E+10 5.92E+10	-0.41 -3.008 -3.021 -3.008 -2.959 -2.855 -2.642 0.94 0.39 0.4 0.4 0.4	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.89E+04 4.95E+02 3.78E+03 3.76E+03 3.76E+03 3.76E+03	removed
R77 R78 R79 R80	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 100 atm 1000 atm $HNO+H=NO+H_2$ $HNO+OH=NO+H_2O$ 0.01 atm 0.1 atm 0.316 atm 1 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.85E+10 5.92E+10 6.30E+10	$\begin{array}{r} -0.41 \\ -3.008 \\ -3.021 \\ -3.008 \\ -2.959 \\ -2.855 \\ -2.642 \\ 0.94 \\ 0.39 \\ 0.4 \\ 0.4 \\ 0.4 \\ 0.39 \end{array}$	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.89E+04 4.95E+02 3.76E+03 3.76E+03 3.76E+03 3.76E+03 3.76E+03 3.78E+03	removed
R77 R78 R79 R80	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 100 atm 100 atm $HNO+H=NO+H_2$ $HNO+OH=NO+H_2O$ 0.01 atm 0.1 atm 0.316 atm 1 atm 3.16 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.85E+10 5.92E+10 6.30E+10 9.53E+10	$\begin{array}{c} -0.41\\ -3.008\\ -3.021\\ -3.008\\ -2.959\\ -2.855\\ -2.642\\ 0.94\\ 0.39\\ 0.4\\ 0.4\\ 0.4\\ 0.4\\ 0.39\\ 0.34\end{array}$	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.85E+04 4.95E+02 3.78E+03 3.76E+03 3.76E+03 3.76E+03 3.78E+03 3.78E+03 3.93E+03	removed
R77 R78 R79 R80	HNO sub-mechanism NO+H(+M)=HNO(+M) HNO=H+NO 0.1 atm 1 atm 10 atm 100 atm 100 atm 100 atm $HNO+H=NO+H_2$ $HNO+OH=NO+H_2O$ 0.01 atm 0.1 atm 0.316 atm 1 atm 3.16 atm 10 atm	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.85E+10 5.92E+10 6.30E+10 9.53E+10 2.60E+11	$\begin{array}{r} -0.41 \\ -3.008 \\ -3.021 \\ -3.008 \\ -2.959 \\ -2.855 \\ -2.642 \\ 0.94 \\ 0.39 \\ 0.4 \\ 0.4 \\ 0.4 \\ 0.39 \\ 0.34 \\ 0.23 \end{array}$	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.89E+04 4.95E+02 3.78E+03 3.76E+03 3.76E+03 3.76E+03 3.78E+03 3.78E+03 4.41E+03	removed
R77 R78 R79 R80	HNO sub-mechanism $NO+H(+M)=HNO(+M)$ $HNO=H+NO$ $0.1 atm$ $1 atm$ $1 atm$ $10 atm$ $100 atm$ $0.01 atm$ $0.1 atm$ $0.316 atm$ $1 atm$ $3.16 atm$ $10 atm$ $31.6 atm$	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.85E+10 5.92E+10 6.30E+10 9.53E+10 2.60E+11 3.83E+11	$\begin{array}{c} -0.41\\ -3.008\\ -3.021\\ -3.008\\ -2.959\\ -2.855\\ -2.642\\ 0.94\\ 0.39\\ 0.4\\ 0.4\\ 0.4\\ 0.39\\ 0.34\\ 0.23\\ 0.2\end{array}$	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.89E+04 4.95E+02 3.78E+03 3.76E+03 3.76E+03 3.76E+03 3.78E+03 3.78E+03 3.93E+03 4.41E+03 5.10E+03	removed
R77 R78 R79 R80	HNO sub-mechanism $NO+H(+M)=HNO(+M)$ $HNO=H+NO$ $0.1 atm$ $1 atm$ $1 atm$ $10 atm$ $100 atm$ $0.01 atm$ $0.1 atm$ $0.316 atm$ $1 atm$ $3.16 atm$ $10 atm$ $31.6 atm$ $100 atm$	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.82E+10 5.92E+10 6.30E+10 9.53E+10 2.60E+11 3.83E+11 4.18E+10	$\begin{array}{r} -0.41\\ -3.008\\ -3.021\\ -3.008\\ -2.959\\ -2.855\\ -2.642\\ 0.94\\ 0.39\\ 0.4\\ 0.4\\ 0.4\\ 0.39\\ 0.34\\ 0.23\\ 0.2\\ 0.51\end{array}$	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.89E+04 4.95E+02 3.78E+03 3.76E+03 3.76E+03 3.76E+03 3.76E+03 3.78E+03 3.93E+03 4.41E+03 5.10E+03 5.53E+03	removed
R77 R78 R79 R80	HNO sub-mechanism $NO+H(+M)=HNO(+M)$ $HNO=H+NO$ $0.1 atm$ $1 atm$ $1 atm$ $10 atm$ $100 atm$ $0.1 atm$ $0.316 atm$ $1 atm$ $3.16 atm$ $10 atm$ $31.6 atm$ $100 atm$ $HNO+HO_2=HNO_2+OH$	1.52E+15 1.83E+20 2.01E+19 1.83E+20 1.28E+21 5.64E+21 9.71E+21 6.60E+10 6.30E+10 5.82E+10 5.82E+10 5.82E+10 5.92E+10 6.30E+10 9.53E+10 2.60E+11 3.83E+11 4.18E+10 2.00E+03	$\begin{array}{r} -0.41\\ -3.008\\ -3.021\\ -3.008\\ -2.959\\ -2.855\\ -2.642\\ 0.94\\ 0.39\\ 0.4\\ 0.4\\ 0.4\\ 0.39\\ 0.34\\ 0.23\\ 0.2\\ 0.51\\ 2.36\end{array}$	0.00E+00 4.79E+04 4.78E+04 4.79E+04 4.81E+04 4.85E+04 4.89E+04 4.89E+02 3.76E+03 3.76E+03 3.76E+03 3.76E+03 3.78E+03 3.78E+03 3.93E+03 4.41E+03 5.10E+03 5.53E+03 8.98E+03	removed

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	NOx sub-mechanism				
R83	NO+OH=HONO	3.09E+23	-4.17	1.62E+03	
	0.01 atm	5.02E+21	-4.24	8.99E+02	
	0.1 atm	5.31E+22	-4.24	1.18E+03	
	0.316 atm	1.38E+23	-4.22	1.38E+03	
	1 atm	3.09E+23	-4.17	1.62E+03	
	3.16 atm	5.45E+23	-4.09	1.91E+03	
	10 atm	6.35E+23	-3.97	2.22E+03	
	31.6 atm	3.68E+23	-3.75	2.50E+03	
	100 atm	7.29E+22	-3.41	2.66E+03	
R84	NO ₂ +O=NO+O ₂	2.59E+15	-1.035	2.26E+02	
	DUPLICATE				
R85	$NO_2+O=NO+O_2$	4.24E+16	-0.861	5.09E+04	
	DUPLICATE				
R86	$N_2O+H_2=N_2+H_2O$	7.00E+12	0	3.25E+04	
	HONO sub-mechanism				
R87	HNO+OH=HONO+H	1.48E+03	2.72	4.55E+03	
	0.01 atm	1.06E+03	2.76	4.44E+03	
	0.1 atm	1.09E+03	2.75	4.45E+03	
	0.316 atm	1.18E+03	2.74	4.48E+03	
	1 atm	1.48E+03	2.72	4.55E+03	
	3.16 atm	2.71E+03	2.64	4.77E+03	
	10 atm	9.67E+03	2.49	5.25E+03	
	31.6 atm	5.31E+04	2.29	6.06E+03	
	100 atm	1.03E+05	2.24	6.95E+03	
R88	HONO+H=NO ₂ +H ₂	1.89E+03	2.83	1.42E+03	
R89	HONO+H=NO+H2O	4.30E+09	0.98	4.07E+03	
	0.01 atm	3.91E+09	0.99	4.05E+03	
	0.1 atm	3.93E+09	0.99	4.05E+03	
	0.316 atm	3.97E+09	0.99	4.05E+03	
	1 atm	4.30E+09	0.98	4.07E+03	
	3.16 atm	7.04E+09	0.92	4.23E+03	
	10 atm	2.60E+10	0.76	4.74E+03	
	31.6 atm	7.91E+10	0.64	5.52E+03	
	100 atm	2.79E+10	0.8	6.15E+03	
R90	HONO+NH2=NH3+NO2	3.17E+02	2.83	-3.57E+03	