



COMBUSTION OF LIQUID AMMONIA, ASSISTED BY PLASMA  
DISCHARGES, AS A NOVEL AND CLEAN ENERGY CONVERSION  
METHOD

# Deliverable D2.1

Detailed kinetic modeling of plasma-NH<sub>3</sub>  
combustion and experimental validation

|                          |                                                                                                   |
|--------------------------|---------------------------------------------------------------------------------------------------|
| Responsible partner:     | Lund University                                                                                   |
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## Project Profile

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## Executive Summary

The present report, entitled “**D2.1- Detailed kinetic modeling of plasma-NH<sub>3</sub> combustion and experimental validation,**” is the first deliverable of the WP2 (NH<sub>3</sub> combustion kinetics and liquid NH<sub>3</sub> combustor development) and relates to T2.1 – NH<sub>3</sub> combustion kinetics and modeling (M1-M18).

The main goal of T2.1 was to provide a detailed and accurate kinetic mechanism and perform reliable modeling studies for NO<sub>x</sub> prediction and control in NH<sub>3</sub> combustion applications. Initial requirements and relevant literature were assessed, and a detailed mechanism for thermal modeling was developed based on the chemiluminescence signatures of NH<sub>3</sub>+various oxidizer flames. The kinetic model was validated against fundamental combustion properties such as flame structure, laminar flame speed, ignition delay, and speciation during pyrolysis and oxidation. Several measurements, such as flame structure, laminar burning velocity of NH<sub>3</sub> flames with various oxidizers, were carried out at the division of combustion physics, LU, and additional data were taken from reported experimental measurements of NH<sub>3</sub> combustion. In addition, the developed chemical model was compared with predictions from several kinetic mechanisms reported in the literature, and the possible reasons for agreements/disagreements in model predictions were discussed thoroughly.

Subsequently, a non-equilibrium NH<sub>3</sub> plasma-combustion model was developed at UoB, integrating thermal and plasma kinetic effects. A Cantera-based C++ 0D plasma solver, CanPlasKin, was implemented as a unified reactor model where neutral combustion chemistry, plasma species kinetics, electron density evolution, and the gas-phase energy equation are solved simultaneously within a single ODE system. The solver employs a hybrid approach combining cross-section-based and electron-temperature-based formulations for electron-impact reaction rates, enabling computationally efficient simulations suitable for CFD coupling. It also provides an automated reaction pathway generator that identifies dominant reaction channels and key intermediates governing plasma-assisted NH<sub>3</sub> oxidation. The solver was validated against reported experimental data for plasma-assisted hydrogen oxidation and ignition delay times in H<sub>2</sub>/O<sub>2</sub>/He mixtures, showing good agreement over a wide temperature range. Further, the development of a new reduced plasma-chemical kinetic mechanism that will be used for CFD-based simulations within CAIPIRINH<sub>3</sub>A is underway. This will serve as the central kinetic framework for all subsequent modelling activities in WP2 (T2.2) and WP3 (T3.2), ensuring methodological consistency.

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## Table of Abbreviations

| Abbreviation                        | Definition                                             |
|-------------------------------------|--------------------------------------------------------|
| <b>LU</b>                           | Lund University                                        |
| <b>UoB</b>                          | University of Birmingham                               |
| <b><math>\Phi</math></b>            | Equivalence ratios                                     |
| <b>NO<sub>x</sub></b>               | Nitrogen oxide                                         |
| <b>ppm</b>                          | Parts per million                                      |
| <b>HAB</b>                          | Height above the burner                                |
| <b>LBV (<math>S_L</math>)</b>       | Laminar burning velocity                               |
| <b><math>S_{L0}</math></b>          | Laminar burning velocity at reference condition        |
| <b><math>T_u</math></b>             | Unburnt mixture temperature                            |
| <b><math>T_{u0}</math></b>          | Unburnt mixture temperature at the reference condition |
| <b><math>\alpha</math></b>          | Temperature coefficient                                |
| <b><math>E_a</math></b>             | Activation energy                                      |
| <b>R</b>                            | Gas constant                                           |
| <b>CH<sub>3</sub>NO<sub>2</sub></b> | Nitromethane                                           |
| <b>LFA</b>                          | Local field approximation                              |
| <b>EEDF</b>                         | Electron energy distribution function                  |
| <b><math>T_e</math></b>             | Electron temperature                                   |
| <b><math>k(T_e)</math></b>          | Electron-Impact Rate Coefficients                      |
| <b>RDP</b>                          | Reaction path diagram                                  |

# 1 Introduction

## 1.1 Scope

The combustion of liquid fuels occurs in the gaseous phase, making kinetic modeling an essential predictive tool for combustor design, scaling, and optimization. While NH<sub>3</sub> pyrolysis and oxidation have been investigated over five decades<sup>1,2</sup> and many NH<sub>3</sub> oxidation detailed kinetic models were since constructed, current models are only suitable for predicting specific experimental conditions. For example, in recent studies of the oxidation of NH<sub>3</sub>/O<sub>2</sub>/Ar mixtures<sup>3</sup>, it was shown that all models failed to reproduce N<sub>2</sub>O profiles for the investigated experimental conditions. Similar<sup>4,5</sup> studies showed significant overpredictions in maximum concentrations of N<sub>2</sub>O and NO<sub>2</sub> in lean, stoichiometric, and rich flames were found in NH<sub>3</sub>/H<sub>2</sub>/O<sub>2</sub>/Ar and NH<sub>3</sub>/O<sub>2</sub>/Ar mixtures under various pressure ranges.

Lately, several studies of chemiluminescence from NH<sub>3</sub>/air, NH<sub>3</sub>/H<sub>2</sub>/air and NH<sub>3</sub>/CH<sub>4</sub>/air turbulent combustion were carried out, aiming at optimization of the process mostly in terms of exhaust NO<sub>x</sub> in the flue gases<sup>6</sup>. Correlations between emission intensities from OH\*, CH\*, NH\* and NH<sub>2</sub>\* and nitric oxide (NO<sub>x</sub>) formation were found promising<sup>7</sup>, therefore dedicated searches for suitable ratios of chemiluminescence reflecting mixture composition, equivalence ratio and stretch were performed in laminar NH<sub>3</sub>/CH<sub>4</sub>/air, NH<sub>3</sub>/H<sub>2</sub>/air, NH<sub>3</sub>/air and turbulent NH<sub>3</sub>/CH<sub>4</sub>/air flames. These empirical observations, however, have not been supported by kinetic modelling due to the lack of appropriate sub-mechanisms for all registered excited species.

While prior studies have been confined to non-plasma environments, plasma is known to significantly alter ammonia flame luminosity and chemistry<sup>8</sup>. Therefore, inclusion of plasma kinetics into chemical kinetics is essential for a complete understanding and optimization of ammonia combustion. CAIPIRINH<sub>3</sub>A directly addresses the current scarcity of such mechanisms as **plasma kinetic mechanisms in pure ammonia and its mixtures are scarce in literature**<sup>9,10</sup>, despite several works dedicated to NH<sub>3</sub> synthesis<sup>11</sup>. Recently, CAIPIRINH<sub>3</sub>A partners modelled the non-equilibrium plasma assisted combustion in NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub>/He and NH<sub>3</sub>/H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures<sup>12,13</sup> by coupling the open-source Boltzmann equation solver, ZDPlaskin<sup>14</sup>, with Cantera codes<sup>15</sup>. The former solves the chemical reaction during the combustion, while the later code integrates the ODEs of thermal reactions. A further objective is to advance these models by refining these foundational kinetic parameters and extending their validation to a wider range of conditions.

<sup>1</sup> Shah, Zubair Ali, et al., *International Journal of Hydrogen Energy* 51 (2024): 354-374.

<sup>2</sup> Elbaz, Ayman M., et al., *Fuel Communications* 10 (2022): 100053.

<sup>3</sup> Alturaifi, Sulaiman A., Olivier Mathieu, and Eric L. Petersen, *Fuel Communications* 10 (2022): 100050.

<sup>4</sup> Osipova, Ksenia N., et al., *Combustion and Flame* 246 (2022): 112419.

<sup>5</sup> Osipova, Ksenia N., Oleg P. Korobeinichev, and Andrey G. Shmakov, *International Journal of Hydrogen Energy* 46.80 (2021): 39942-39954.

<sup>6</sup> Zhu, Xuren, Jianguo Du, Zhou Yu, Yi-Bing Cheng, and Yu Wang, *Energy & Fuels* 38, no. 1 (2023): 43-60.

<sup>7</sup> Matsugi, Akira, *Combustion and Flame* 269 (2024): 113706.

<sup>8</sup> Choe, J. and Sun, W., *Proc. Combust. Inst.* 39 (2023) 5439-5446.

<sup>9</sup> Faingold, Galia, and Joseph K. Lefkowitz., *Proceedings of the Combustion Institute* 38.4 (2021): 6661-6669.

<sup>10</sup> Taneja, Taresh Sanjeev, Praise Noah Johnson, and Suo Yang. *Combustion and Flame* 245 (2022): 112327.

<sup>11</sup> Engelmann, Yannick, et al., *ACS Sustainable Chemistry & Engineering* 9.39 (2021): 13151-13163.

<sup>12</sup> Shahsavari, Mohammad, et al. *Combustion and Flame* 245 (2022): 112368.

<sup>13</sup> Shahsavari, Mohammad, et al. "Synergistic effects of nanosecond plasma discharge and hydrogen on ammonia combustion." *Fuel* 348 (2023): 128475.

<sup>14</sup> Pancheshnyi, S., et al. "Computer code zdplaskin." *University of Toulouse, LAPLACE, CNRS-UPS-INP, Toulouse, France* (2008).

<sup>15</sup> Goodwin, David G., et al. "Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes." *Zenodo* (2018).

Within this deliverable (D2.1) of CAIPIRINH<sub>3</sub>A, a novel detailed kinetic model for plasma-NH<sub>3</sub> combustion is developed that interconnects the thermal combustion model and plasma kinetic model. The detailed chemical kinetic model was developed at LU and the development of non-equilibrium plasma kinetics in NH<sub>3</sub> and incorporation with the thermal kinetic model is being developed at UoB. The developed thermal combustion model was validated against various experimental data of fundamental combustion properties such as ignition delay, flame speed and flame structure from in-house experiments and literature data. It was found that the present model exhibits a very good agreement with available measurements of laminar burning velocity within  $\pm 2$  cm/s, ignition delay times within  $\pm 27$ -40%, and major species concentrations in flames, including NO<sub>x</sub> within  $\pm 30\%$ .

In the next phase, a unified 0D plasma solver named **CanPlasKin** was developed in which thermal combustion chemistry, plasma species kinetics, electron density evolution, and gas-phase energy equation are solved simultaneously within a single ODE system. CanPlasKin enables the implementation of complex electron-impact reaction rate expressions in which the reaction coefficients are defined as explicit algebraic functions of the electron temperature ( $T_e$ ). In this framework, electron-impact reactions can be expressed in analytical form (e.g., exponential–logarithmic polynomial functions of  $T_e$ ), such as those in Taneja et al.<sup>16</sup>.

$$k(T_e) = A \cdot \exp(a + b \log(T_e) + \frac{c}{T_e} + \frac{d}{T_e^2} + \frac{e}{T_e^3})$$

This formulation allows direct integration of the governing ordinary differential equations without the need to call an external Boltzmann solver (e.g., BOLSIG+) or perform repeated cross-section-based electron kinetics calculations during runtime. As a result, the computational cost is significantly reduced, enabling fast time integration, which is essential when coupling the plasma solver with CFD simulations. In addition, to analyse the coupling between plasma-driven activation and thermal combustion chemistry in the NH<sub>3</sub>/air/plasma system, time-resolved Reaction Path Diagrams (RPDs) were generated automatically using the Cantera Reaction Path library. Furthermore, this structure provides a robust foundation for the systematic development of reduced plasma-chemical reaction mechanisms in subsequent project stages (WP3), where computational efficiency and numerical stability are essential. The first version of the plasma mechanism used for the implementation is provided as supplementary material to ensure transparency and reproducibility.

The developed solver in D2.1 serves as the first predictive simulations of plasma-assisted NH<sub>3</sub> combustion to implement for a novel area of mixture stratification effects on plasma and thermal chemistry by other CAIPIRINH<sub>3</sub>A partner, paving the way for practical spray combustion application. The objectives achieved in the present deliverables are:

- **Developed a Novel Kinetic Model:** Developed a detailed accurate kinetic model for NH<sub>3</sub> combustion that resolves significant current discrepancies with experimental flame speed, ignition delay and flame structure data, incorporating recent advances in chemiluminescence sub-mechanisms.
- **Developed NH<sub>3</sub>-Plasma Combustion Solver (CanPlasKin):** Developed a unified solver that integrates plasma kinetics and chemical kinetics in 0D with Cantera C++ for plasma-assisted NH<sub>3</sub> combustion.
- **Development of reduced plasma-chemical kinetics:** Reduced plasma–chemical reaction mechanisms were systematically under development and will be implemented in flow simulations of NH<sub>3</sub> spray combustion to accelerate time integration when coupling plasma solvers with CFD simulations. The resulting global, reduced, and comprehensive NH<sub>3</sub>–plasma combustion models offer strong predictive capability for the design and optimization of advanced NH<sub>3</sub> combustion systems in CAIPIRINH<sub>3</sub>A.

<sup>16</sup> T.S. Taneja, H. Sitaraman, S. Yang, 1D Modeling of Plasma Streamers at Ammonia-Air Flame Conditions, J. Phys. D, 2024

## 1.2 Relation to other tasks and deliverables

The deliverable D2.1 is directly related to different tasks of WP2 and WP3.

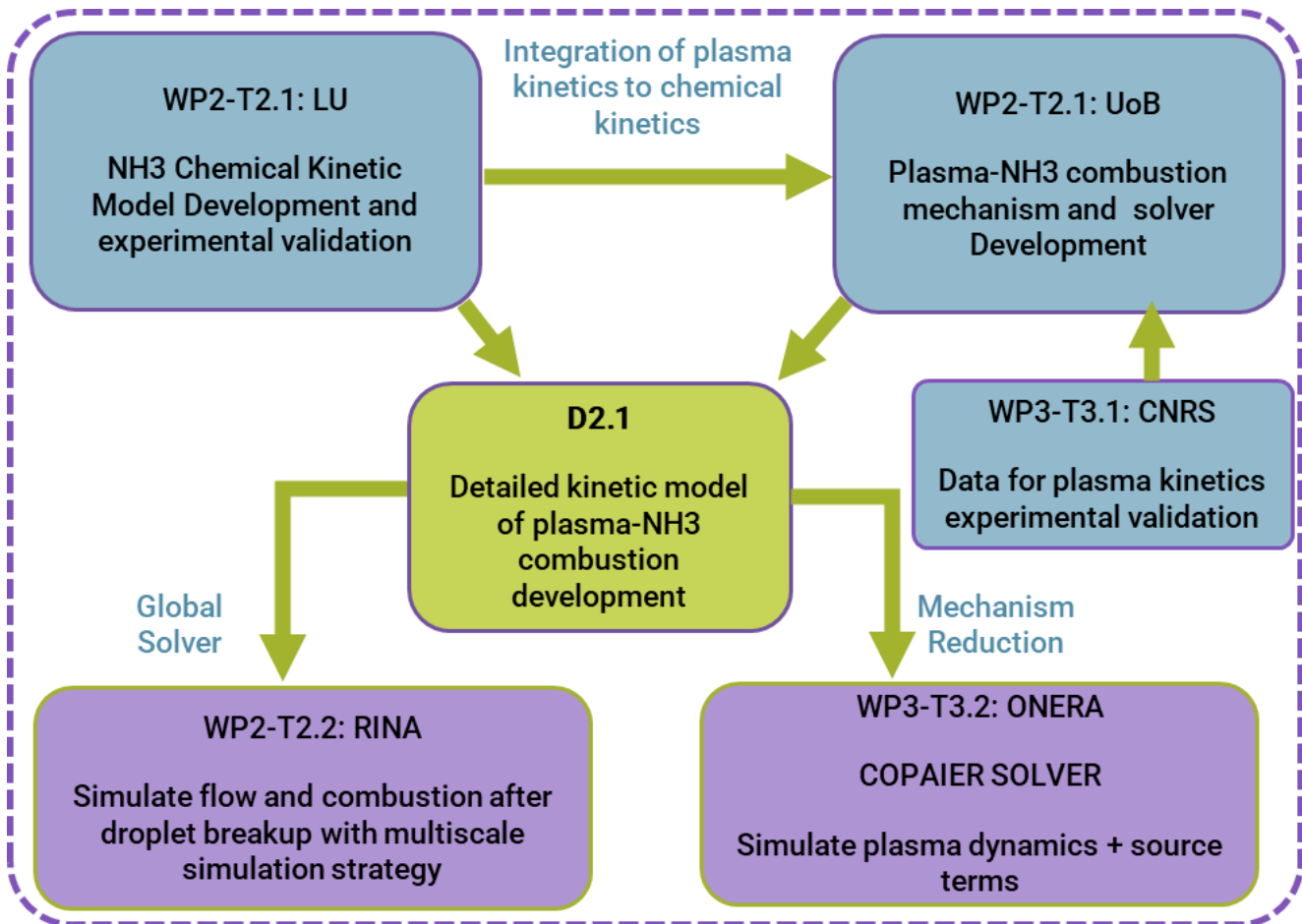


Figure 1: Schematic of the relationship of D2.1 with other work packages in CAIPIRINH3A.

## 1.3 Structure of the deliverable

The structure of D2.1 are divided into the following sections:

- **Section 2** – NH<sub>3</sub> combustion kinetics development and experimental validation
  - 2.1 – Methodology
  - 2.2 – Results
  - 2.3 – Summary of a detailed validated NH<sub>3</sub> chemical kinetic model
- **Section 3** – NH<sub>3</sub>-Plasma combustion kinetics development & modeling
  - 3.1– Integration with plasma kinetics
  - 3.2– Plasma modeling
  - 3.3– Reaction path diagram
- **Section 4** – Outcome
- **Section 5**– Conclusions
- **ANNEX I**: A Detailed Chemical Kinetic Model for NH<sub>3</sub> combustion
- **ANNEX II**: NH<sub>3</sub>-Plasma Combustion Mechanisms and CanPlasKin Solver

## 2 NH<sub>3</sub> combustion kinetics development and experimental validation

### 2.1 Methodology

#### 2.1.1 Chemical kinetic model development

A detailed chemical kinetic model for ammonia combustion is developed at LU describing chemiluminescence in ammonia-fuelled flames<sup>17,18</sup>. The present NH<sub>3</sub> kinetic mechanism has been developed over the years and has passed several iterations. The detailed mechanism consists of 44 species and 428 reactions which include the chemiluminescence signature of various excited species in ammonia-fuelled flames. In addition, the thermodynamic and transport data were also periodically updated from recent literature. The chemical kinetic model was validated over a wide temperature and pressure ranges for NH<sub>3</sub>+various oxidisers pertinent to practical combustion applications.

#### 2.1.2 Experimental validation

The accuracy of the chemical kinetic model requires validation using the fundamental combustion properties, such as laminar burning velocity (LBV), ignition delay time, speciation and flame structure, as shown in the schematic below. The LBV and ignition delay times are global combustion characteristics representing overall reactivity of the mixture, whereas the flame structure and speciation profile are micro-scale combustion characteristics that serve as more stringent validation target. Here, the detailed mechanism was validated across the above-mentioned properties over a wide range of temperature and pressure. The flame structure experiments were conducted in porous-plug McKenna burner at LU and other reported data from the literature. The laminar burning velocity data are obtained from heat flux burner measurements at LU and other types of burners reported in the literature. The ignition delay data from shock tube and speciation profiles from kinetic reactors such as jet-stirred reactor, plug-flow reactor are taken from the literature. A brief discussion of the experimental setup and procedure is given below:

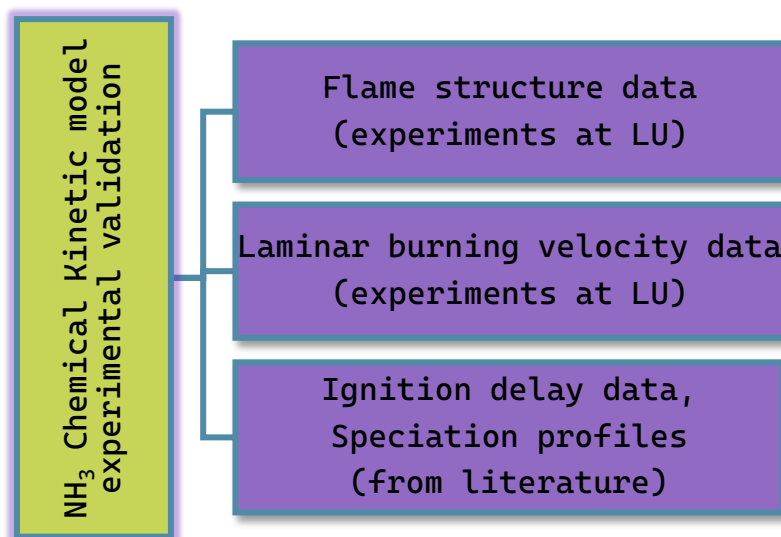


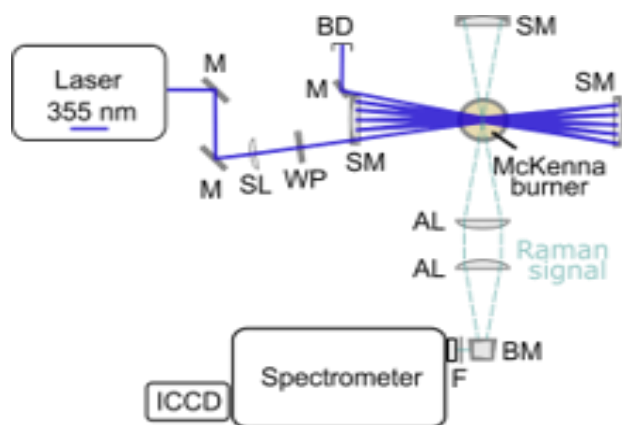
Figure 2: Schematic of the following short outline of experiments and how they helped in the mechanism development

<sup>17</sup> Konnov, Alexander A. "An exploratory modelling study of chemiluminescence in ammonia-fuelled flames. Part 1." *Combustion and Flame* 253 (2023): 112788.

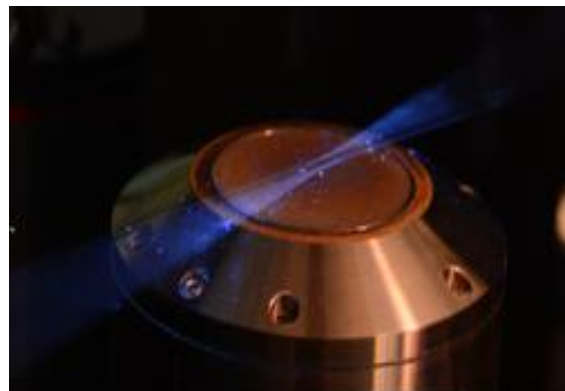
<sup>18</sup> Konnov, Alexander A. "An exploratory modelling study of chemiluminescence in ammonia-fuelled flames. Part 2." *Combustion and Flame* 253 (2023): 112789.

### a) Flame structure measurement using Raman Spectroscopy

The setup employed in the current experiment is based on a multipass system, variations of which have been recently successfully applied to enhance the relatively weak Raman signals to allow for the detection of minor species, as reported in <sup>19</sup>. However, operation at 532 nm wavelength in NH<sub>3</sub> flames leads to LIF, which produces a background signal strong enough to obscure Raman signals, eliminating any possibility of reaction zone measurements. The current work employed a multipass system aligned at 355 nm, with a schematic of it illustrated in Fig.3(a). An Nd:YAG laser operating at 10 kHz repetition rate with an average power of 22 W was used as the light source. The beam was guided into the multipass cavity through an  $f = 70$  cm focusing lens and a mechanical (Thorlabs ELL14) rotational mount housing a  $\lambda/2$  waveplate used to change the laser polarization.



(a)



(b)

Figure 3: (a) Schematic of the Raman spectroscopy setup for flame studies. M: mirror, WP: half-wave plate, SL: spherical lens, M: spherical mirror, AL: achromatic lens, BM: broadband mirror, F: 355 nm notch filter. (b) A photo of the laser beam multipass arrangement over a McKenna burner<sup>19</sup>.

A porous-plug McKenna burner 6 cm in diameter was placed on a translational mount below the two focal points of the multipass cavity, allowing for height adjustment (Fig. 3(b)). The burner was supplied with NH<sub>3</sub>, O<sub>2</sub> and Ar using calibrated mass flow controllers. A stainless-steel stagnation plate, positioned 2 cm above the burner surface, was used to stabilize the premixed flames in the gap 2.5-5 mm above the burner surface, depending on the equivalence ratio. A water bath (Grant GD120) was used to keep the burner cooling water and plug at a constant temperature of 303 K for additional flame stability.

### b) Laminar burning velocity (LBV) measurement using the heat flux method

Experiments in the present study were performed using a heat flux burner setup from Lund University (LU setup)<sup>20</sup>. A schematic of the LU setup is provided in Fig. 4. The setup, LBV determination method and procedures of uncertainty evaluation were introduced by Alekseev et al.<sup>21</sup>. The typical LBV uncertainty for this burner is better than  $\pm 0.3$  cm/s; however, the calibration of the thermal mass flow controllers (MFC) can bring additional uncertainties.

<sup>19</sup> Zubairova, A., Chen, J., Konnov, A. A., & Brackmann, C. (2025). Flame structure study of premixed NH<sub>3</sub>/O<sub>2</sub>/Ar flames using Raman spectroscopy. *Combustion and Flame*, 280, 114382.

<sup>20</sup> Lavadera, Marco Lubrano, and Alexander A. Konnov., *Energy & Fuels* 34.3 (2020): 3725-3742.

<sup>21</sup> Alekseev, Vladimir A., et al., *Combustion Science and Technology* 188.6 (2016): 853-894.

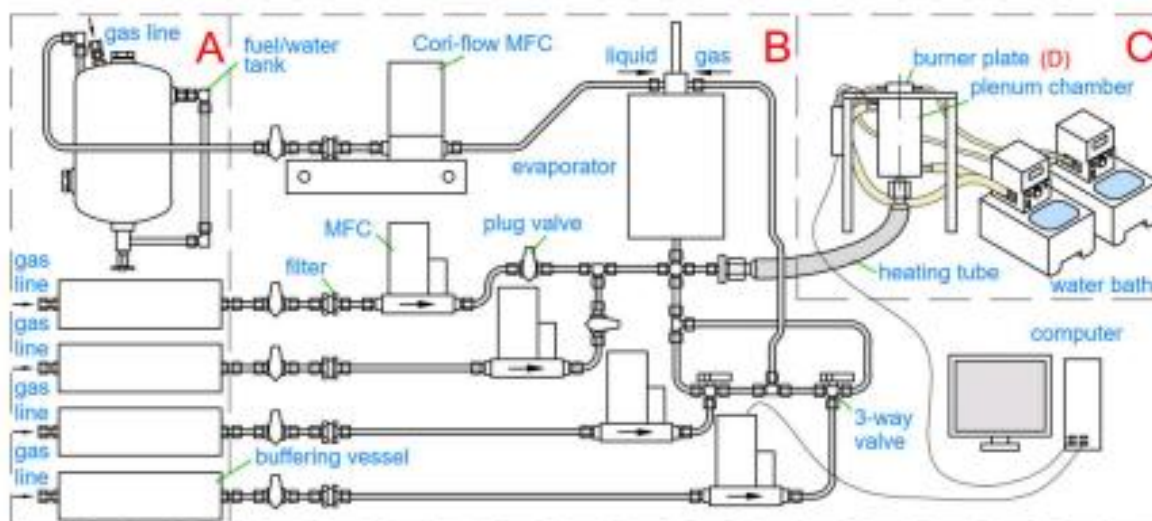


Figure 4: Schematic of a typical heat flux burner experimental setup (not to scale) at Lund University<sup>21,20</sup>.

### 2.1.3 Numerical modeling

All modeling work was performed in ANSYS Chemkin-Pro software (<https://www.ansys.com>), which is designed to simulate the conditions necessary for analysing combustion properties of interest.

- **Laminar burning velocity:** Laminar burning velocities are calculated using the Premix Laminar Flame Speed module of the Chemkin-Pro software. This module assumes a freely propagating adiabatic, premixed, stretch-free flame. Simulations were also often run with the Multicomponent Transport option with optimised Solution Gradients (GRAD) and Solution Curvature (CURV). The thermal diffusion effect and radiation heat loss were accounted for in the simulation.
- **Flame structure:** Flame structure simulations were performed using the Premixed Laminar Burner Stabilized Stagnation Flame model. This module is used to simulate laminar, premixed flames stabilized on a burner, with one inlet for the premixed blend of fuel and oxidizer and another boundary as a wall. Thermal diffusion effect and mixture averaged transport were considered. Boundary conditions such as stagnation plate temperature, simulation axial distance, and mixture inlet velocity were specified to match those in the experiments. Depending on the used detailed kinetic model and the corresponding stiffness of convergence, mesh refinement tolerances for the species profiles were set to 0.02-0.23 for the GRAD parameter and 0.02-0.23 for the CURV parameter. The final grid for the flame contained approximately 100-600 mesh points.
- **Ignition delay:** The Closed Homogeneous Batch Reactor module was used for simulations of shock tubes. Shock tube simulations were performed assuming constant volume and solving the energy equation. Non-ideal boundary conditions were considered as specified in the literature. The ignition delay times are steady-state solutions, and the definition of ignition moments was consistent with those in the literature experiments. Shock tube speciation profiles are transient solutions; the simulation results over time evolution were compared with the experiments.

The present model was also widely validated against detailed kinetic models from literature over a wide temperature and pressure ranges for NH<sub>3</sub>+various oxidisers flame and updated by revisiting the rate constants of several important reactions.

## 2.2 Results

### 2.2.1 Validation of the kinetic model against flame structure measurement of premixed NH<sub>3</sub>/O<sub>2</sub>/Ar flames

Enhanced Raman spectroscopy with multiple laser beam passages is implemented that allows for non-intrusive sensitive detection and quantification of two major nitrogen oxide species, NO and N<sub>2</sub>O, in flame with detection limits of 600 and 500 ppm, respectively in a burner stabilized stagnation flat NH<sub>3</sub> flame<sup>19</sup>. All the measurements were carried out in NH<sub>3</sub>/O<sub>2</sub>/Ar flames in a porous-plug McKenna burner to involve only NO<sub>x</sub> reactions from fuel-bound nitrogen at equivalence ratios ( $\Phi=0.8, 1.0, 1.2$ ). In addition to flame structure data of NO, N<sub>2</sub>O, and other major species such as NH<sub>3</sub>, O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub> mole fractions, and temperature profile, were also measured for all three flame conditions. The acquired data have the potential to assist with the validation of the present NH<sub>3</sub> chemical kinetic model. Figures 5 and 6 show the measured NO and N<sub>2</sub>O profiles in three flames along the height above the burner covering the premixed, reaction and post reaction zone.

The present kinetic mechanism was validated against the measured species and temperature profile and compared with predictions of four NH<sub>3</sub> chemical kinetic mechanisms from the literature<sup>22,23,24</sup>. The possible reasons for disagreements in model predictions were discussed. Predictions of the present kinetic model qualitatively and quantitatively agree with the measurements, both in terms of the gradients and of the major species concentrations in the fresh mixture and the products, and the observed mismatch with the modelling is primarily due to the differences in burning velocity predictions.

Compared with minor species such as NO, N<sub>2</sub>O and, to a degree, H<sub>2</sub>, the behaviour of the most abundant species (O<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>O) of reactants and products is well determined, and all simulation mechanisms agree within 1%. Thus, validation against these data is not the purpose of the present study, and the major species are used as a tool for quantification of the minor species. The observed discrepancies between experimental results and modelling predictions only affected the concentrations evaluated for minor species N<sub>2</sub>O and NO within the error margins, which was considered sufficient for the minor species quantification.

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<sup>22</sup> A. Stagni, C. Cavallotti, S. Arunthanayothin, Y. Song, O. Herbinet, F. Battin-Leclerc, T. Faravelli, *React. Chem. Eng.*, 5 (2020), pp. 696-711.

<sup>23</sup> X.L. Han, Z.H. Wang, Y. He, Y.Q. Zhu, K.F. Cen, *Combust. Flame*, 213 (2020), pp. 1-13.

<sup>24</sup> X.Y. Zhang, S.P. Moosakutty, R.P. Rajan, M. Younes, S.M. *Combust. Flame*, 234 (2021), 111653.

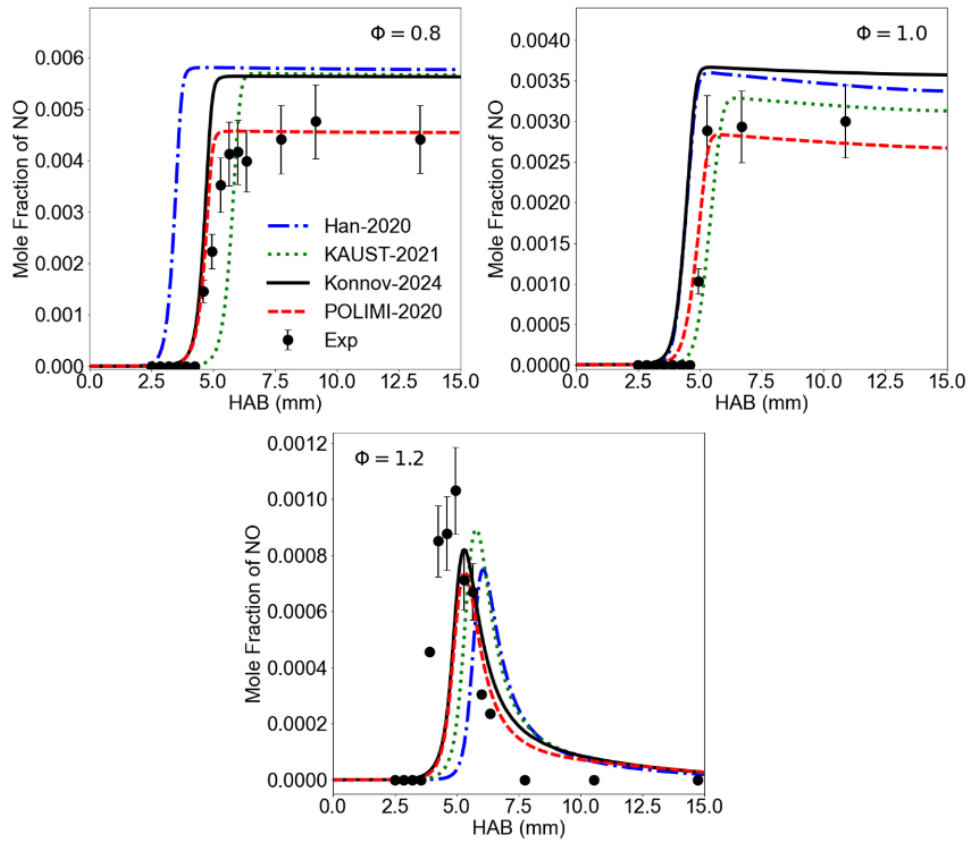


Figure 5: NO mole fraction change with HAB. Experimental values (circles) compared with predictions of the four kinetic models (lines) including the present model<sup>19</sup>.

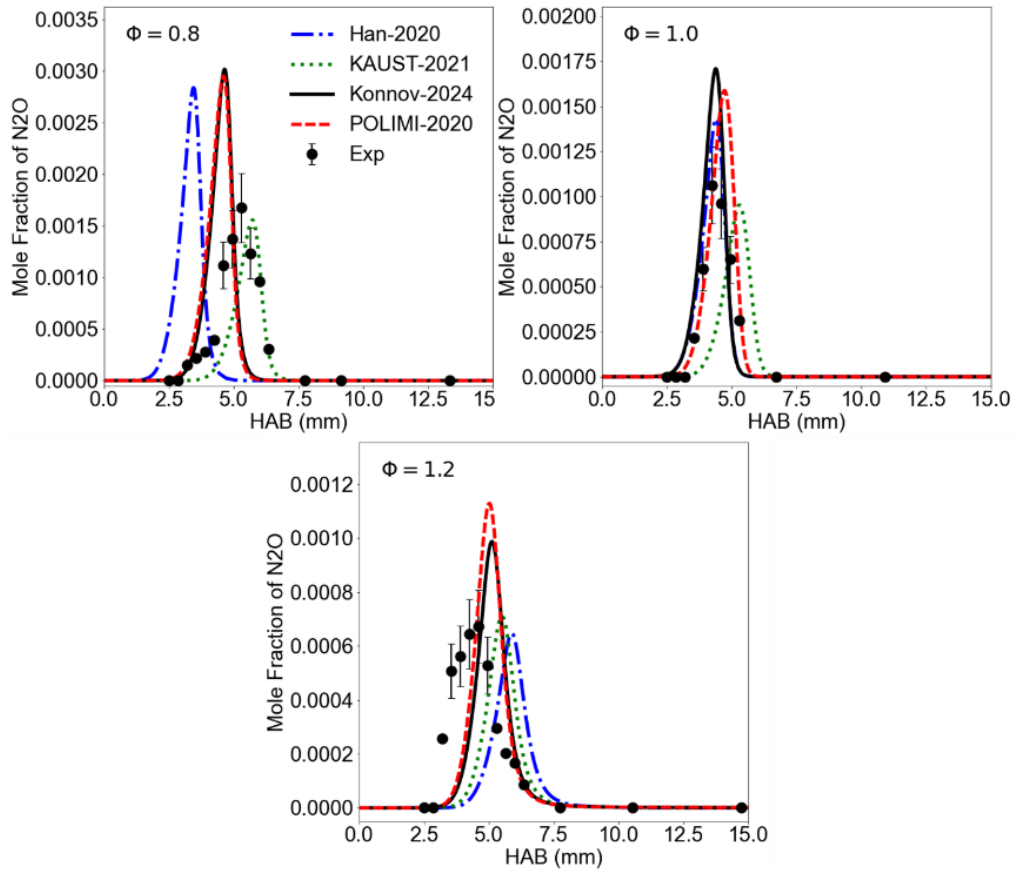


Figure 6: N<sub>2</sub>O change with HAB. Experimental values (circles) compared with predictions of the four kinetic models (lines) including the present model<sup>19</sup>.

## 2.2.2 Validation of the kinetic model against the laminar burning velocity of NH<sub>3</sub>+ various oxidizers flames

The LBV measurements for (NH<sub>3</sub> + H<sub>2</sub>) + air mixture at 1 atm<sup>25</sup>, 3 and 5 atm<sup>26,27</sup>, for NH<sub>3</sub> + O<sub>2</sub> + Ar mixtures<sup>28</sup>, as well as NH<sub>3</sub> + air mixtures at various temperatures<sup>29</sup>, are compared with the simulations using the present model, as shown in Fig. 7. The present model captures these data generally well at both atmospheric and elevated pressure, as well as NH<sub>3</sub> + air mixtures within  $\pm 2$  cm/s<sup>30</sup>.

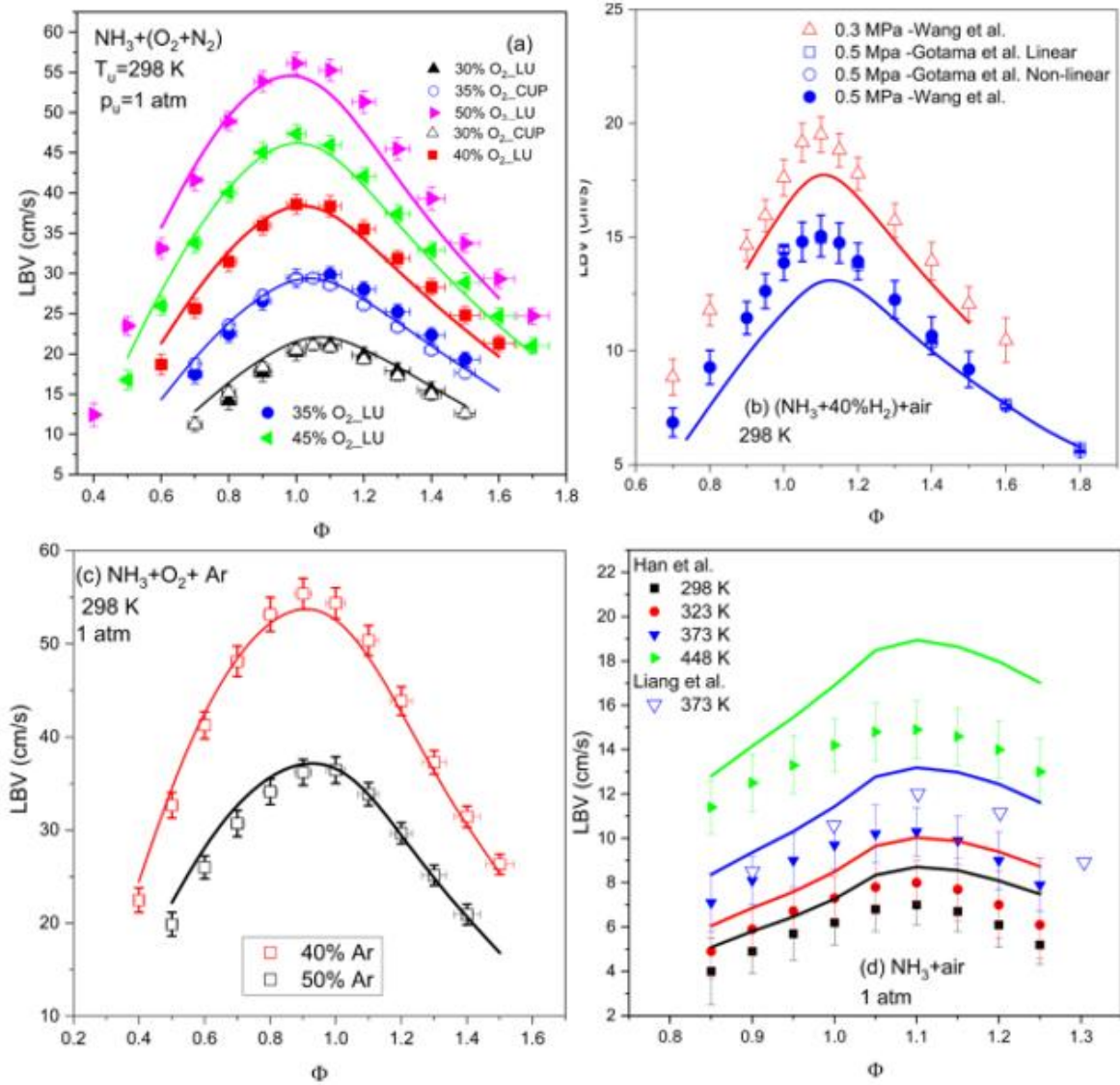


Figure 7: The present kinetic model<sup>130</sup> compares with LBV as function of  $\Phi$  (a) (NH<sub>3</sub>+H<sub>2</sub>)+air flames at 298 K, 1 atm,  $x_{H_2}$ = 0.15, 0.25, 0.35 and 0.4. (b) (0.6NH<sub>3</sub>+0.4H<sub>2</sub>)+air mixture at 3 and 5 atm, (c) NH<sub>3</sub>+O<sub>2</sub>+Ar mixtures for 40% and 50% Ar dilution, (d) NH<sub>3</sub>+air mixture at 298 K, 323 K, 373 K, and 448 K.

<sup>25</sup> Han, X., Wang, Z., Costa, M., Sun, Z., He, Y., & Cen, K. (2019). *Combustion and Flame*, 206, 214-226.

<sup>26</sup> Wang, Shixing, et al. *Combustion and Flame* 221 (2020): 270-287.

<sup>27</sup> Gotama, Gabriel J., et al. *Combustion and Flame* 236 (2022): 111753.

<sup>28</sup> Chen, J., Lavadera, M. L., & Konnov, A. A. (2023), *Combustion and Flame*, 255, 112930.

<sup>29</sup> Liang, Bo, et al. *International Journal of Hydrogen Energy* 48.53 (2023): 20225-20237.

<sup>30</sup> Chen, Jundie, Xinlu Han, and Alexander A. Konnov, *Fuel* 385 (2025): 134017.

Further, a comprehensive analysis of the relationship between the NH<sub>3</sub> laminar burning velocity ( $S_L$ ) and unburnt mixture temperature ( $T_u$ ) was conducted across a large span of unburnt mixture temperature from 298 K to 800 K, through the analysis of literature experimental data and simulation results<sup>31</sup>. The 40%H<sub>2</sub>+60%NH<sub>3</sub>+air flames at 1 atm were selected for analysis, representing the only available literature measurements with > 500 K conditions. To achieve this, simulations using multiple models, including the present model, were carried out along with analysis, before which the evaluation of the high-data uncertainties from the literature measurements were also performed. Seven kinetic models<sup>28,32,33,34,35,36,37</sup> were adopted in the simulation and those from Shrestha<sup>34</sup>, Stagni<sup>33</sup>, Han<sup>31</sup>, NUIG<sup>36</sup>, and KAUST<sup>37</sup> well reproduce the experimental  $S_L$  data within uncertainties. For example, fig. 8 shows the laminar burning velocities of 40%H<sub>2</sub>+60%NH<sub>3</sub>+air flames at 1 atm across a broad range of unburnt temperatures from 298 K to 923 K, with panels (a) to (c) corresponding to equivalence ratios = 0.8, 1.0, and 1.2, respectively. In each panel, the data were plotted as  $\ln S_L$  vs.  $\ln T_u$ , demonstrating  $\ln S_L$  increases approximately linearly with  $\ln T_u$  across the broad range of temperatures investigated, with the  $R^2$  value of the linear fit exceeding 0.9959, irrespective of the model used and the equivalence ratio  $\Phi$ . It reveals that existing correlations, with their originally defined constants, fail to precisely capture the  $S_L$  vs.  $T_u$  dependence across the wide temperature range, attributing this to a rise in the overall activation energy with increasing  $\Phi$ . This work is important as it proposed a feasible strategy for future investigation of the laminar burning velocities with broad unburnt temperature range, i.e., (1) substituting high measurements with oxygen enrichment experiments, (2) validating the models using the experimental data or model updating considering the sensitivities of overall activation energy, and (3) simulating the directly or fitting parameters to correlations for interpolation/extrapolation, reducing computational costs.

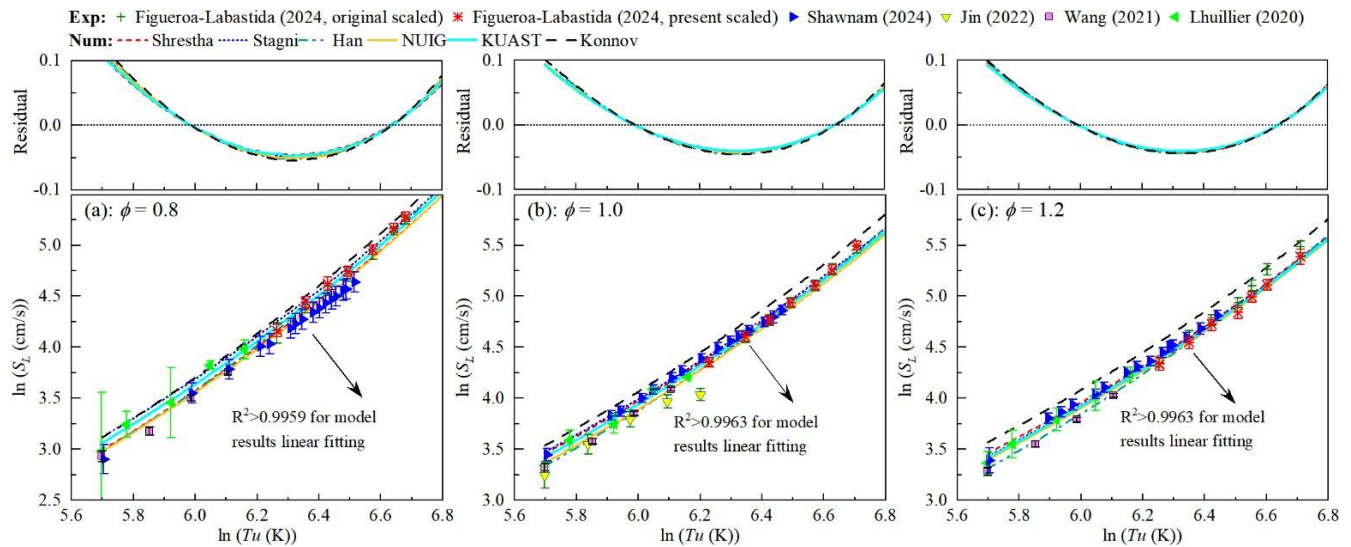


Figure 8: Relationship of  $\ln S_L$  vs.  $\ln T_u$  for 40%H<sub>2</sub>+60%NH<sub>3</sub>+air flames at 1 atm with a broad  $T_u$  range, where linear fitting results were presented with residuals<sup>31</sup> (a)  $\Phi = 0.8$ , (b)  $\Phi = 1.0$ , and (c)  $\Phi = 1.2$ .

<sup>31</sup> Han, X., & Konnov, A. A. (2025), *Combustion and Flame*, 275, 114117.

<sup>32</sup> X. Han, Z. Wang, B. Zhou, Y. He, Y. Zhu, K. Cen, *Appl. Energy Combust. Sci.*, 15 (2023), 100160.

<sup>33</sup> Stagni, Alessandro, et al., *Chemical Engineering Journal* 471 (2023): 144577.

<sup>34</sup> Shrestha, Krishna Prasad, et al., *Proceedings of the Combustion Institute* 38.2 (2021): 2163-2174.

<sup>35</sup> Zhang, Xiaoyuan, et al., *Combustion and Flame* 234 (2021): 111653.

<sup>36</sup> Zhou, Shangkun, et al., *Combustion and Flame* 248 (2023): 112536.

<sup>37</sup> Zhu, Yuxiang, et al., *Combustion and Flame* 260 (2024): 113239.

### 2.2.3 Validation of the kinetic model against the laminar burning velocity of NH<sub>3</sub> + fuel blend as NO precursor

NH<sub>3</sub> combustion with an oxidizer different from the ambient air can reveal distinct chemistry of NO<sub>x</sub> formation, which, together with low reactivity, is one of the major obstacles in the direct deployment of ammonia as a practical fuel. In the present investigation, ammonia was blended with nitromethane (CH<sub>3</sub>NO<sub>2</sub>), which was used as a nitric oxide (NO) precursor<sup>38</sup>. The laminar burning velocities of NH<sub>3</sub>+CH<sub>3</sub>NO<sub>2</sub> blends burning in the air were measured using the heat flux method at LU. The NH<sub>3</sub> mole fraction in the fuel blends varied from 0-80%, covering fuel-lean to fuel-rich conditions, at a fixed initial temperature of 338 K and 1 atm. The primary objective is to investigate the interaction of NH<sub>3</sub> and NO, while the study also contributes to the understanding of CH<sub>3</sub>NO<sub>2</sub> fuel combustion and validate with the kinetic model. An updated model based on previous iterations of the authors was proposed and compared against the present LBV measurements, together with the models of Mathieu et al.<sup>39</sup> and Shrestha et al.<sup>40</sup>. It was found that both the present and the model of Mathieu et al. give very good predictions for the present (CH<sub>3</sub>NO<sub>2</sub>+NH<sub>3</sub>)+air flames as observed from fig. 9(a). In Fig. 9(b), it can be observed that the model by Mathieu et al. poorly predicts the LBV of NH<sub>3</sub>+(NO+N<sub>2</sub>) mixtures; the model of Shrestha et al. over-predicts the LBV for mixtures with 40% and 50% NO in the oxidizer, especially on the fuel-rich side. However, the performance of the present model varies across different NO percentages and equivalence ratios. It generally provides good predictions but under-predicts LBV on the fuel-lean side with 70% NO in the oxidizer, and over-predicts LBV on the fuel-lean side for 50% NO in the oxidizer.

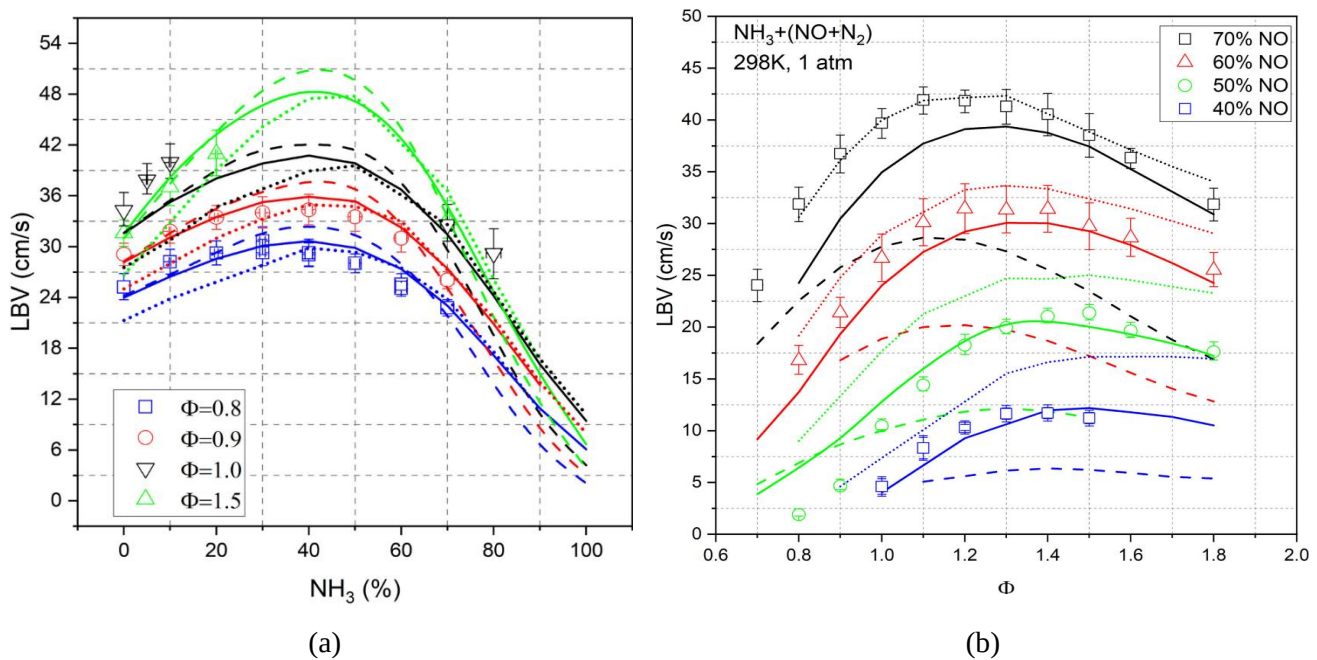


Figure 9: Experimental (symbols) and simulated (lines)<sup>38</sup> (a) LBV of (CH<sub>3</sub>NO<sub>2</sub>+NH<sub>3</sub>)+air mixtures with various NH<sub>3</sub>% in the fuel, at Φ= 0.8, 0.9, 1.0, and 1.5. (b) LBV of NH<sub>3</sub>+(NO+N<sub>2</sub>) mixtures. Experiments are from<sup>41</sup>, Solid lines: the present model, dashed lines: the model of Mathieu et al.<sup>39</sup> dotted lines: the model of Shrestha et al.<sup>40</sup>.

<sup>38</sup> Chen, J., & Konnov, A. A. (2025), *Combustion and Flame*, 277, 114230.

<sup>39</sup> O. Mathieu, B. Giri, A.R. Agard, T.N. Adams, J.D. Mertens, E.L. Petersen, *Fuel*, 182 (2016), pp. 597-612.

<sup>40</sup> K.P. Shrestha, L. Seidel, T. Zeuch, G. Moréac, P. Dagaut, F. Mauss, *Fuel*, 289 (2021), 11986.

<sup>41</sup> Monnier, Noé, et al. , *Proceedings of the Combustion Institute* 40.1-4 (2024): 105266.

## 2.2.4 Validation of the kinetic model against ignition delay time and speciation of NH<sub>3</sub>

Ignition delay times (IDT) of NH<sub>3</sub> (+H<sub>2</sub>) + O<sub>2</sub> + Ar mixtures, which were measured by Mathieu et al.<sup>42</sup> and Chen et al.<sup>43</sup> is compared with the present model as shown in Fig. 10 (a) and (b). The present model shows excellent agreement with high-temperature ignition delay times for a wide range of pressure and hydrogen fraction. The profiles of NH<sub>3</sub> during ammonia decomposition are stringent for helping scrutinize the pyrolysis chemistry. Fig. 11 shows the present model predictions compared with the NH<sub>3</sub> pyrolysis at low (2096 K, blue), medium (2258 K, grey), and high temperatures (2487 K, red) history from Alturaifi et al.<sup>44</sup>. The present model reproduces the NH<sub>3</sub> time history accurately against the experiment.

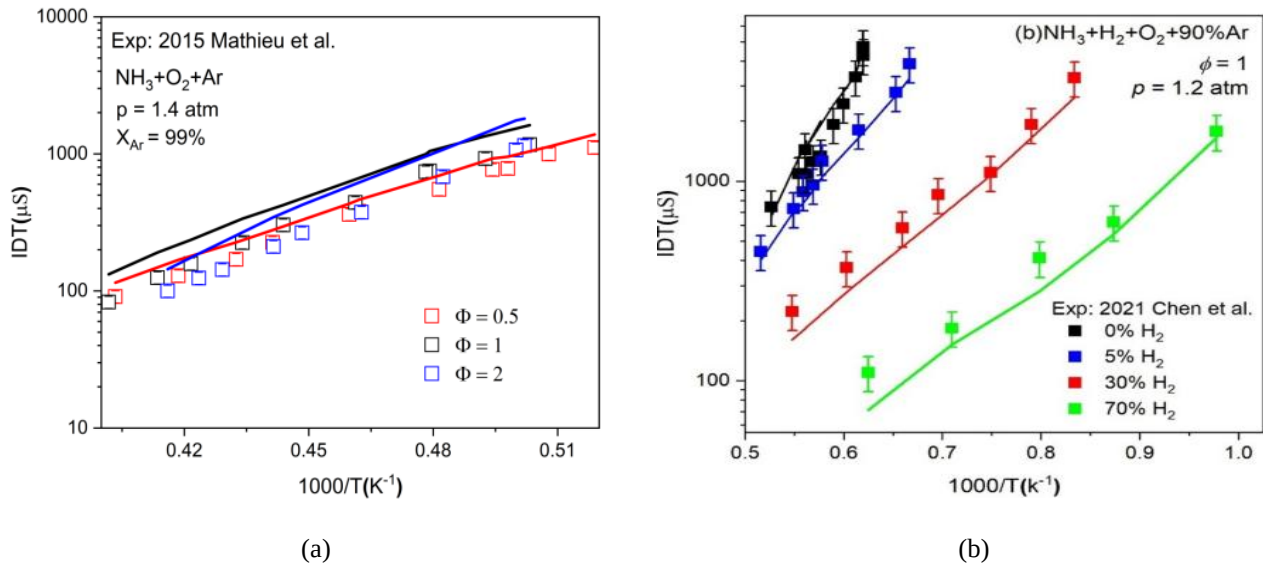


Figure 10: Predictions of the present model for high-temperature IDT from (a) Mathieu et al.<sup>42</sup> for NH<sub>3</sub> + O<sub>2</sub> + Ar mixtures at 1.4 atm,  $\Phi = 0.5-2$ , and (b) Chen et al.<sup>43</sup> for NH<sub>3</sub> + H<sub>2</sub> + O<sub>2</sub> + Ar mixture at  $\Phi = 1$ , 1.2 atm, H<sub>2</sub> = 0-70%. Experiment (symbols) and simulation (lines)<sup>30</sup>.

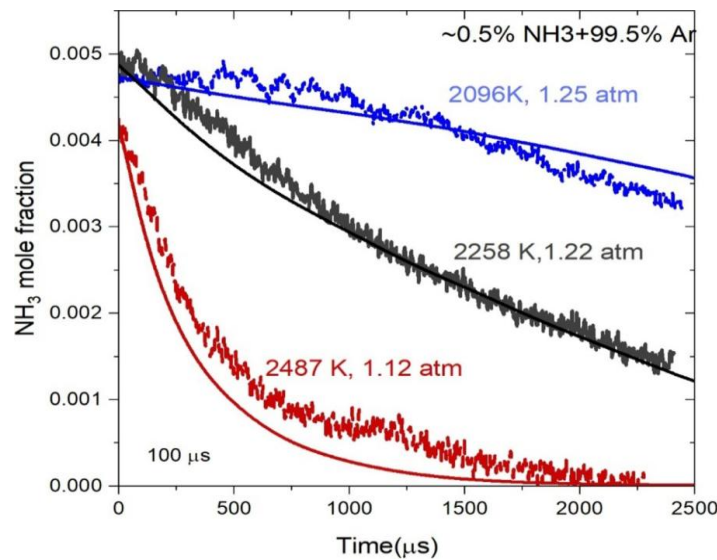


Figure 11: Experimental (symbols) data from<sup>44</sup> and simulated (lines) with the present model of for NH<sub>3</sub> speciation profiles for a mixture of ~0.5% NH<sub>3</sub> in Ar<sup>30</sup>.

<sup>42</sup> Mathieu, O., & Petersen, E. L. (2015), *Combustion and flame*, 162(3), 554-570.

<sup>43</sup> Chen, J., Jiang, X., Qin, X., & Huang, Z. (2021), *Fuel*, 287, 119563.

<sup>44</sup> Alturaifi, S. A., Mathieu, O., & Petersen, E. L. (2022). *Combustion and Flame*, 235, 111694.

## 2.3 Summary of a detailed validated NH<sub>3</sub> chemical kinetic model

- A detailed and accurate chemical kinetic model of NH<sub>3</sub> combustion is developed in LU, which consists of kinetic, thermal and transport data, which is provided in CAIPIRINH<sub>3</sub>A's ZENODO and a link to it is provided in the Annex I.
- The developed model is validated rigorously across various fundamental combustion properties such as flame structure, laminar burning velocity, ignition delay time and speciation data from experiments. This resulted in an accurate, robust and advanced chemical kinetic model for NH<sub>3</sub>-combustion.
- Several measurements, such as flame structure and laminar burning velocity, were carried out at LU combustion division, and other data were taken from reported experimental measurements of NH<sub>3</sub> combustion from the literature for model validation.
- In addition, the present model was compared with predictions of several kinetic mechanisms from the literature and the possible reasons for agreements/disagreements in model predictions were discussed thoroughly.
- It is found that the agreement with available measurements of laminar burning velocity is within  $\pm 2$  cm/s<sup>30,31</sup>, ignition delay times are within  $\pm 27$ -40%<sup>19,30</sup> and major species concentrations in flames within  $\pm 30\%$ <sup>19</sup>.
- The concentrations for NO and N<sub>2</sub>O were well reproduced by the present models<sup>19</sup> within the experimental error margins within  $\pm 5\%$  and  $\pm 10\%$  respectively.
- The developed advanced chemical kinetics simulation tool will be used to parametrize fundamental combustion and emission characteristics by other partners within CAIPIRINH<sub>3</sub>A.

## 3 NH<sub>3</sub>-Plasma combustion kinetics development & modeling

### 3.1 Integration with plasma kinetics

The plasma-combustion coupling strategy implemented in this work builds upon established 0D gas-plasma kinetic frameworks reported in the literature, particularly the operator-splitting approach of Lefkowitz et al. (2015)<sup>45</sup>, the unified ODE structure of ChemPlasKin (Shao et al., 2024)<sup>46</sup>, and the electron-temperature-based rate formulation used by Taneja et al. (2024)<sup>10</sup>.

Similar to Lefkowitz et al.<sup>45</sup>, the present solver adopts the local field approximation (LFA), whereby electron-impact reaction rates depend on the local reduced electric field ( $E/N$ ) through the electron energy distribution function (EEDF). The solver is structured as a unified 0D reactor in which neutral combustion chemistry, plasma species kinetics, electron density evolution, and gas-phase energy equation are solved simultaneously within a single ODE system.

The solver developed at UoB supports two alternative formulations for electron-impact reaction rates:

1. **Cross-section-based formulation:** If electron collision cross-sections are provided, the solver can compute reaction rate coefficients from the EEDF under LFA conditions. In this mode, precomputed or dynamically evaluated Boltzmann solutions can be used to determine electron transport and reaction coefficients.
2. **Algebraic  $T_e$ -based formulation:** The solver allows direct implementation of electron-impact reaction rate coefficients as explicit algebraic functions of electron temperature ( $T_e$ ), following the methodology

<sup>45</sup> Lefkowitz Joseph K, Guo Peng, Rousso Aric, Ju Yiguang., Phil Trans R Soc A 2015;373(2048):20140333, Publisher: Royal Society.

<sup>46</sup> Shao, Xiao, Deanna A. Lacoste, and Hong G. Im., *Applications in Energy and Combustion Science* 19 (2024): 100280.

reported by Taneja et al.<sup>10</sup>. In this formulation, reaction rates are expressed analytically (e.g., polynomial–logarithmic exponential functions of  $T_e$ ), without evaluating cross-sections during runtime.

In the present deliverable, the second approach is primarily employed. The electron temperature is not obtained from solving an electron energy balance equation (as in local energy approximation models), nor is the Boltzmann equation solved online (as in ChemPlasKin). Instead,  $T_e$  is derived from the mean electron energy obtained from precomputed BOLSIG-generated lookup tables as a function of reduced electric field ( $E/N$ ). These tables are generated offline and embedded into the solver.

This hybrid strategy offers several advantages:

- It retains the physical consistency of LFA-based plasma kinetics.
- It avoids the computational overhead of solving the Boltzmann equation during runtime.
- It enables rapid time integration, which is critical for future CFD coupling within WP3.
- It provides a flexible framework for systematic plasma–chemical mechanism reduction in subsequent project stages.

Compared to ChemPlasKin, which solves the Boltzmann equation online within a unified ODE framework, the present solver achieves significantly reduced computational cost when algebraic rate expressions are employed. At the same time, it maintains the capability to revert to cross-section-based rate evaluation when higher-fidelity plasma kinetics are required.

A further key capability of the developed solver is its dynamic coupling with the Cantera Reaction Path Diagram (RPD) library. At user-specified time instances during the simulation, the solver automatically calls the Reaction Path Diagram routines and generates reaction pathway diagrams for selected elements or species. This functionality enables detailed, time-resolved analysis of:

- Coupling between thermal reactions and electron-impact reactions,
- Dominant production and consumption pathways,
- Energy transfer routes between plasma and neutral chemistry,
- Identification of rate-controlling steps under plasma-assisted conditions.

This is significant because plasma-assisted combustion involves strongly coupled electron-driven and thermally driven reaction networks. Automated reaction path analysis allows systematic identification of dominant reaction channels and key intermediate species, which is essential for:

- Understanding the mechanistic interaction between plasma kinetics and thermal NH<sub>3</sub> oxidation chemistry,
- Quantifying the relative contribution of electron-impact versus thermal pathways,
- Guiding sensitivity analysis and mechanism simplification,
- Developing reduced plasma–chemical kinetic mechanisms in the coming months.

The generation of reduced mechanisms is critical for subsequent CFD simulations within WP3, where computational efficiency and numerical stability are essential. The automated reaction path analysis implemented here provides the mechanistic foundation required for that reduction process. The quantitative validation of this plasma–combustion solver is presented in Section 3.2.

## 3.2 Plasma modeling

### 3.2.1 Solver Validation

#### In H<sub>2</sub>/O<sub>2</sub> Mixture

To validate the developed 0D plasma–chemical kinetic solver, simulations were performed for the plasma-assisted oxidation of hydrogen in an undiluted lean H<sub>2</sub>/O<sub>2</sub> mixture ( $\phi = 0.01$ ), following the study by Snoeckx et

al.<sup>47</sup>. In that work, detailed plasma kinetics were applied to investigate hydrogen oxidation rates in a dielectric barrier discharge (DBD) reactor under constant pressure and temperature conditions. The reference case considers plasma power levels of 0-20 W. Figure 12 compares the present UoB solver (CanPlasKin) predictions with the results reported by Snoeckx et al. for the hydrogen oxidation rate as a function of gas temperature. The overall agreement between the two models is very good across the investigated temperature range. The solver successfully reproduces the temperature-dependent enhancement of hydrogen oxidation under plasma conditions, capturing both the magnitude and the trend of the oxidation rate at 10 W and 20 W plasma power levels. In particular, the present model accurately predicts the strong plasma-induced acceleration of H<sub>2</sub> consumption at lower gas temperatures, where thermal oxidation alone would be negligible. The increase in oxidation rate with increasing plasma power is also well reproduced, demonstrating that the implemented electron-impact reaction pathways and energy deposition modelling are consistent with established plasma-assisted combustion kinetics. Minor deviations observed at higher temperatures can be attributed to differences in mechanism implementation details, such as treatment of vibrational excitation, energy partitioning assumptions, and discharge representation. Nevertheless, the close quantitative agreement confirms that the developed solver reliably captures the coupling between electron-driven chemistry and thermal hydrogen oxidation.

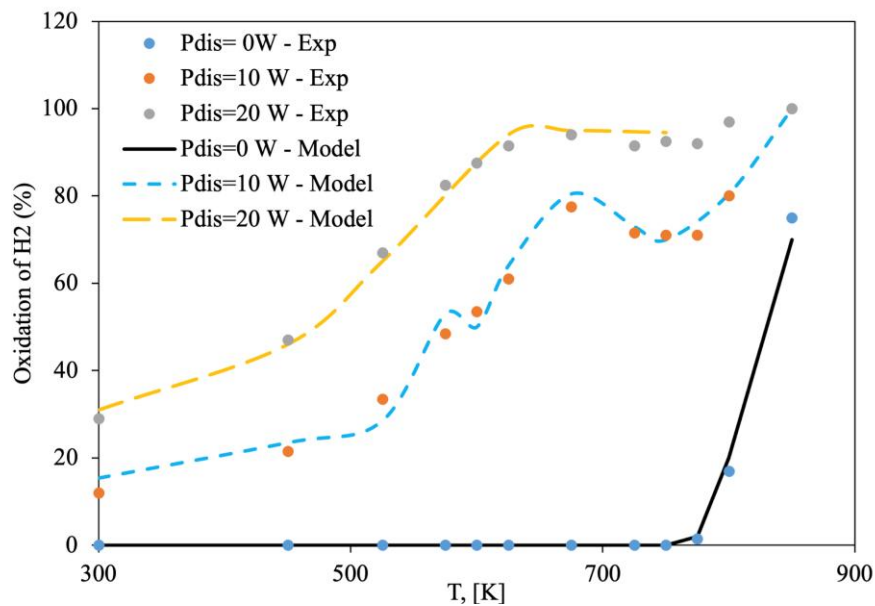


Figure 12: Comparison of UoB solver predictions with Snoeckx et al.<sup>47</sup> for plasma-assisted H<sub>2</sub> oxidation rates in an undiluted lean H<sub>2</sub>/O<sub>2</sub> mixture at ( $\phi = 0.01$ ) at 0-20 W plasma power.

### In H<sub>2</sub>/O<sub>2</sub>/He mixture

Figure 13 provides additional validation of the developed UoB plasma-chemical kinetic solver (CanPlasKin) through comparison with the results reported by Mao et al.<sup>48</sup> for plasma-assisted ignition in a diluted H<sub>2</sub>/O<sub>2</sub>/He mixture (H<sub>2</sub>/O<sub>2</sub>/He = 0.1667/0.0833/0.75) at atmospheric pressure over a range of initial gas temperatures. This test case represents a widely used benchmark configuration for evaluating plasma-assisted ignition kinetics due to the strong coupling between electron-impact reactions and radical chain branching in highly diluted hydrogen mixtures. As shown in Fig. 13, the present solver reproduces the ignition behaviour reported by Mao et al.<sup>48</sup> with good quantitative agreement across the temperature range. In particular, the model captures the characteristic reduction in ignition delay at lower temperatures induced by plasma activation. The close agreement between the present simulations and literature results confirms that the implemented electron-impact reaction set and energy coupling treatment correctly represent the fundamental plasma-assisted ignition pathways in diluted hydrogen systems. This validation therefore further demonstrates the robustness of the CanPlasKin framework for

<sup>47</sup> Snoeckx, Ramses, et al. , *Combustion and Flame* 242 (2022): 112205.

<sup>48</sup> Mao, Xingqian, et al., *Combustion and Flame* 206 (2019): 522-535.

simulating plasma-enhanced combustion chemistry and supports its application to more complex fuel systems such as NH<sub>3</sub>/air mixtures.

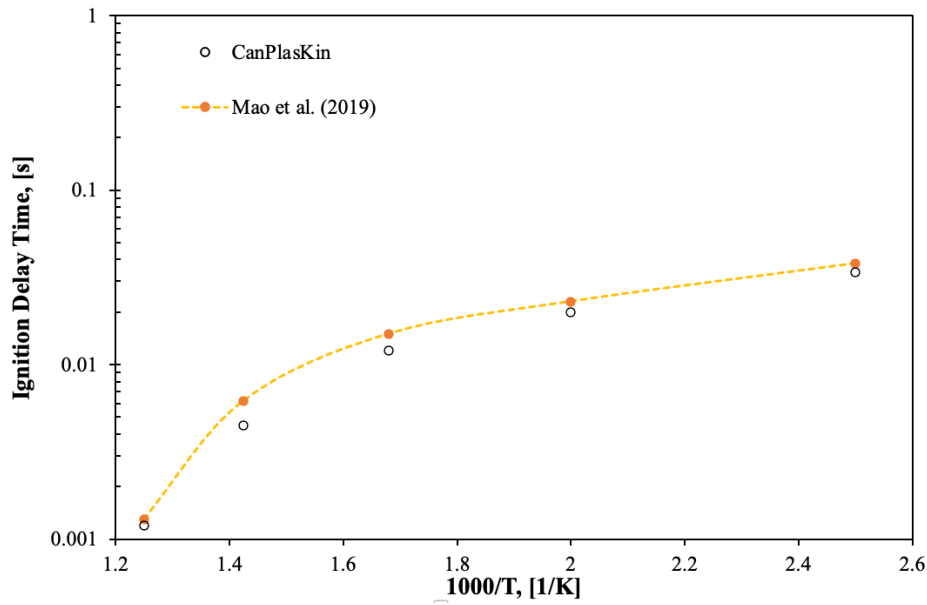


Figure 13: Comparison of UoB solver predictions with Mao et al.<sup>48</sup> for plasma-assisted H<sub>2</sub>/O<sub>2</sub>/He: 0.1667/0.0833/0.75 ignition at atmospheric pressure and different temperatures.

### 3.2.2 NH<sub>3</sub>/Air/Plasma Kinetics – Implementation of T<sub>e</sub>-Based Reduced Mechanism

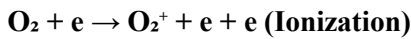
For the plasma-assisted NH<sub>3</sub>/air oxidation modelling, the reduced plasma–chemical kinetic mechanism reported by Taneja et al.<sup>10</sup> was adopted as a reference framework. The reaction mechanism used by Taneja et al. is itself based on the detailed plasma–chemical study of Zhong et al.<sup>49</sup>, in which electron-impact reactions, excited species chemistry, and NO<sub>x</sub> formation pathways were rigorously analysed for NH<sub>3</sub>/O<sub>2</sub> systems under nanosecond plasma discharges. Taneja et al.<sup>10</sup> reformulated selected electron-impact reaction rate coefficients from the Zhong et al. mechanism into explicit algebraic functions of electron temperature ( $T_e$ ), enabling efficient integration within combustion-oriented solvers without repeated evaluation of electron cross-sections.

#### Functional Form of Electron-Impact Rate Coefficients:

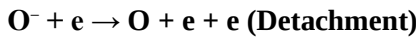
Taneja et al., electron-impact reaction rates are expressed in exponential–polynomial form as:

$$k(Te) = A \cdot \exp\left(a + b \log(Te) + \frac{c}{Te} + \frac{d}{Te^2} + \frac{e}{Te^3}\right)$$

For example:



$$k(Te) = (1.0 \times 10^6) \cdot \exp\left(-3.81089916 \times 10^1 + 6.55328174 \times 10^{-1} \log(Te) - \frac{2.28204343 \times 10^5}{Te} + \frac{1.72569010 \times 10^8}{Te^2} + \frac{1.82072297}{Te^3}\right)$$



$$k(Te) = 2.0 \times 10^{-7} \exp\left(\frac{63824.75}{Te}\right)$$

<sup>49</sup> H. Zhong et al., Combustion and Flame 256 (2023) 112948.

These compact expressions allow direct evaluation of rate coefficients without cross-section integration.

### **Custom Reaction-Rate Library Implementation in Cantera**

To support such generalised algebraic rate forms, a new custom reaction-rate module was implemented within the Cantera framework (source codes are provided). This extension enables:

- Logarithmic and polynomial dependencies on  $T_e$ ,
- Inverse power-law terms ( $1/T_e$ ,  $1/T_e^2$ ,  $1/T_e^3$ ),
- User-defined analytical expressions through the mechanism file,
- Seamless integration within the unified plasma–chemical ODE system.

This implementation significantly enhances Cantera’s capability for plasma–combustion modelling and enables flexible switching between cross-section-based and algebraic  $T_e$ -based formulations.

### **Identification of Discrepancies in Published Rate fits and proposed correction functional forms**

During implementation and verification of the Taneja et al.<sup>10</sup> rate expressions, a systematic comparison was conducted against the original electron-impact reaction rates reported by Zhong et al.<sup>49</sup>, from which the reduced mechanism was derived.

As shown in the comparison figures 14 and 15, notable discrepancies were identified between:

The algebraic fits provided by Taneja et al.<sup>10</sup>, and the original electron-impact rate coefficients from Zhong et al.<sup>49</sup>.

For example:

- In the dissociative attachment reaction ( $e + O_2 \rightarrow O + O^-$ ), the  $T_e$ -dependent behaviour of the fitted expression deviates significantly from the original rate profile at moderate and high  $T_e$ .

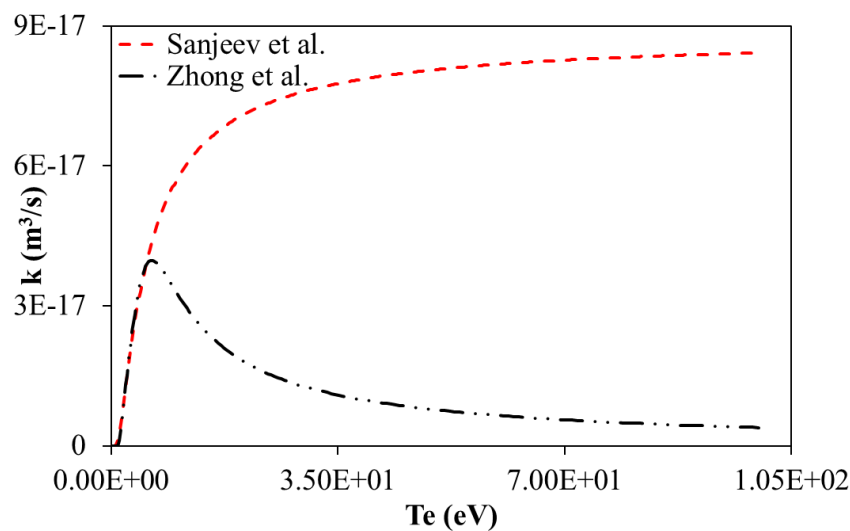


Figure 14: Comparison of electron-impact dissociative attachment rate coefficients ( $e + O_2 \rightarrow O + O^-$ ) from Taneja et al.<sup>16</sup> and the original Zhong et al.<sup>49</sup> dataset, highlighting discrepancies in  $T_e$ -dependent behaviour.

- For oxygen ionization ( $e + O_2 \rightarrow O_2^+ + 2e$ ), deviations become pronounced at elevated electron temperatures, leading to systematic over- or under-prediction relative to the original cross-section-based rates.

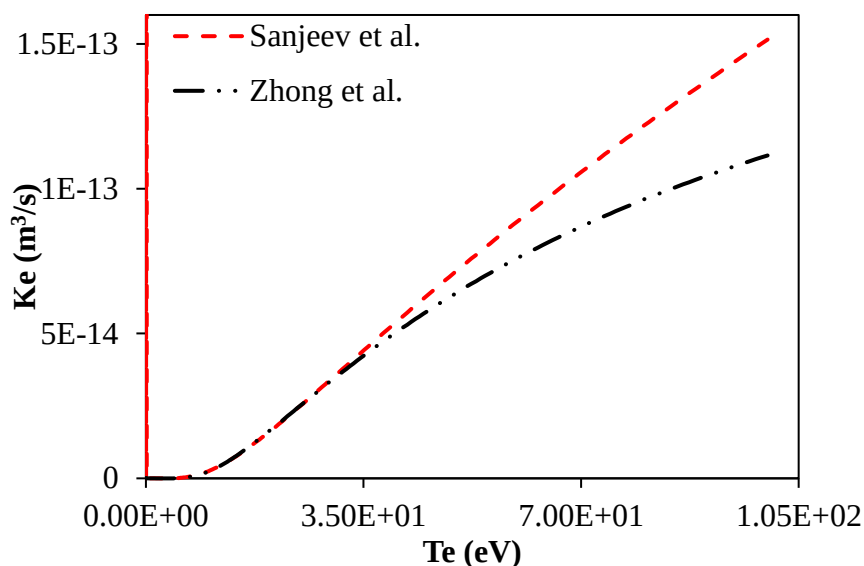


Figure 15: Comparison of electron-impact ionization rate coefficients ( $e + O_2 \rightarrow O_2^+ + 2e$ ) from Taneja et al.<sup>16</sup> and Zhong et al.<sup>49</sup>, showing deviations of the fitted  $T_e$ -based formulation at elevated electron temperatures.

Similar discrepancies were identified for N<sub>2</sub> and NH<sub>3</sub> ionization and dissociation channels. Consequently, careful verification and correction of selected rate coefficients were performed to ensure consistency with the underlying electron-impact physics. The CanPlasKin solver links along with original mechanism and UoB corrections are provided in the Annex II. UoB is currently undertaking further validation of the implemented reduced NH<sub>3</sub>/air/plasma mechanism against available experimental data from the literature, including plasma-assisted ignition, oxidation, and NO<sub>x</sub> formation studies. Additional validation will also be performed using experimental datasets to be generated and shared by CAIPIRINH3A project partners in the forthcoming months. This systematic benchmarking will ensure that the reduced formulation maintains predictive accuracy across a broad range of plasma and thermochemical conditions.

In parallel, UoB is developing a new reduced plasma–chemical kinetic mechanism derived directly from detailed coupled electron–thermal kinetic models for the NH<sub>3</sub>/air/plasma system. This next-generation reduced mechanism will be constructed using reaction path analysis, sensitivity analysis, and mechanistic consistency checks to ensure accurate representation of dominant plasma–thermal interaction pathways while maintaining computational efficiency. The new reduced mechanism is expected to be delivered in the coming months and will form a critical component for CFD-based simulations within CAIPIRINH3A.

### 3.3 Reaction path diagram

To elucidate the coupling between plasma-driven activation and thermal combustion chemistry in the NH<sub>3</sub>/air/plasma system, time-resolved Reaction Path Diagrams (RPDs) were automatically generated using the integrated Cantera Reaction Path library. The diagrams were extracted at representative times corresponding to a typical instant inside the discharge pulse and a typical instant during the inter-pulse phase. Both cases were analyzed to distinguish plasma-dominated and thermally dominated regimes and to identify the dominant pathways governing NH<sub>3</sub> oxidation and NO<sub>x</sub> formation.

#### Inside the Pulse (Plasma-Dominated Regime)

During the discharge pulse, electron-impact processes dominate the reaction network. The reaction path diagram corresponding to this phase shows:

- Rapid activation of stable molecules through electron collisions,
- Generation of excited species and radicals,
- Strong coupling between oxygen activation and nitrogen chemistry.

- Oxygen Activation

Within the pulse:

- O<sub>2</sub> undergoes rapid excitation and dissociation.
- O(<sup>1</sup>D) and atomic O are strongly produced.
- Ion-related pathways and detachment reactions contribute to radical formation.

The oxygen pathway is highly centralised around excited O(<sup>1</sup>D) and atomic O, which redistribute flux toward:

- OH formation,
- H<sub>2</sub>O production,
- Radical pool enhancement.

These species act as immediate radical sources for nitrogen oxidation.

- Nitrogen–Hydrogen Network

The nitrogen pathway inside the pulse reveals:

- Direct coupling between NH<sub>3</sub> and radical species (H, OH, O),
- Strong NH<sub>3</sub> → NH<sub>2</sub> flux,
- Enhanced NH<sub>2</sub> → NH conversion driven by radical attack.

Electron-driven chemistry significantly enhances the formation of NH<sub>2</sub> and NH intermediates. The pulse, therefore, acts as an activation stage, rapidly increasing the concentration of reactive NH<sub>x</sub> species.

NO<sub>x</sub>-related intermediates (HNO, HONO, HNO<sub>2</sub>) are initiated during the pulse but are not yet governed by purely thermal control. Instead, they are influenced by the transient radical surge produced by electron-impact activation.

Overall, inside the pulse:

- Electron reactions dominate,
- Radical production is maximized,
- Excited and charged species play an active role,
- The system is strongly non-equilibrium.

When the electric field collapses and electron-impact reactions cease, the system transitions into the inter-pulse regime. If thermal reactions are excluded, the reaction network rapidly weakens:

- Electron-driven activation pathways vanish,
- Excited species decay,
- Ion chemistry collapses,
- Radical fluxes diminish significantly.

Under this condition, the network lacks sustained radical propagation. The plasma pulse alone cannot maintain continuous oxidation without thermal chemistry. This demonstrates that plasma activation must be followed by thermally driven reactions to sustain combustion enhancement. In fig. 16(a) comparison of RPD of NH<sub>3</sub>/air oxidation with plasma-only chemistry (no-thermal reactions) at typical time inside the pulse and in inter-pulse period is shown Fig.16(b).

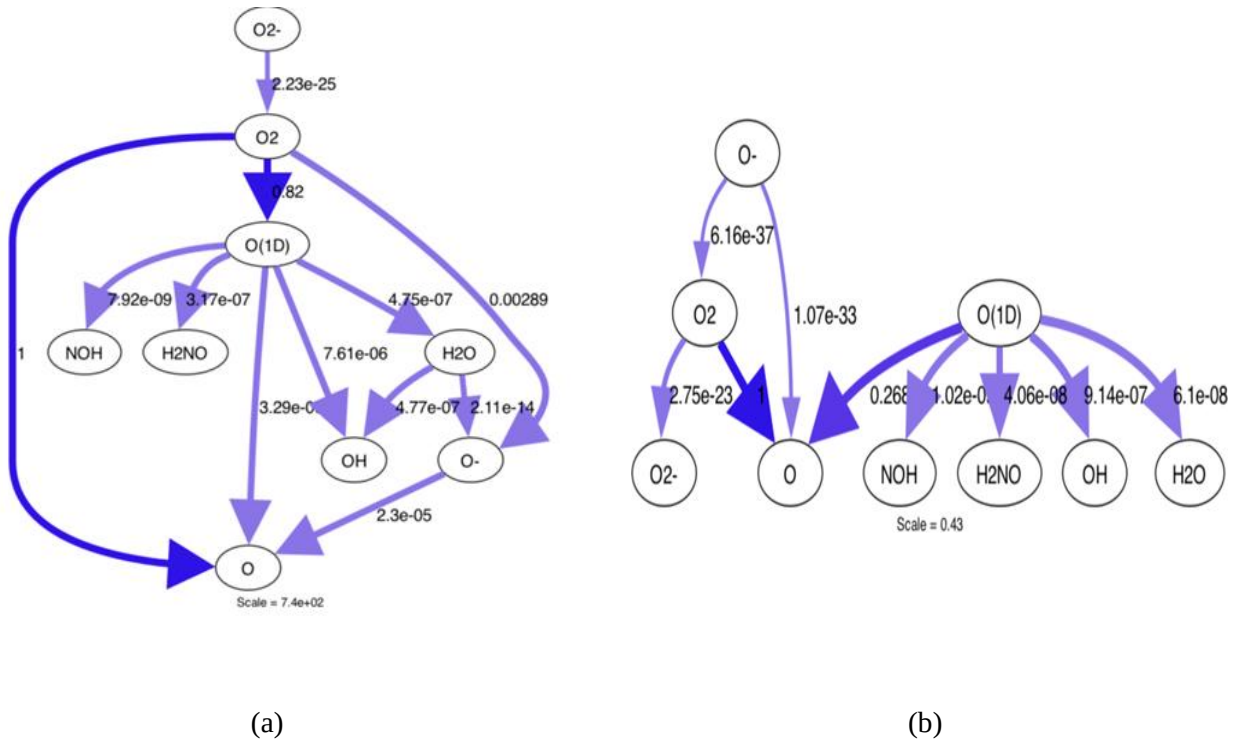


Figure 16: Comparison of Reaction Path Diagram of NH<sub>3</sub>/air oxidation with plasma-only chemistry (no-thermal reactions) at typical time inside the pulse (left) and in inter-pulse period.

## 4 Outcome

Under WP2, the D2.1 have successfully developed a detailed kinetic model for plasma-NH<sub>3</sub> combustion, achieving the primary goal of CAIPIRINH3A.

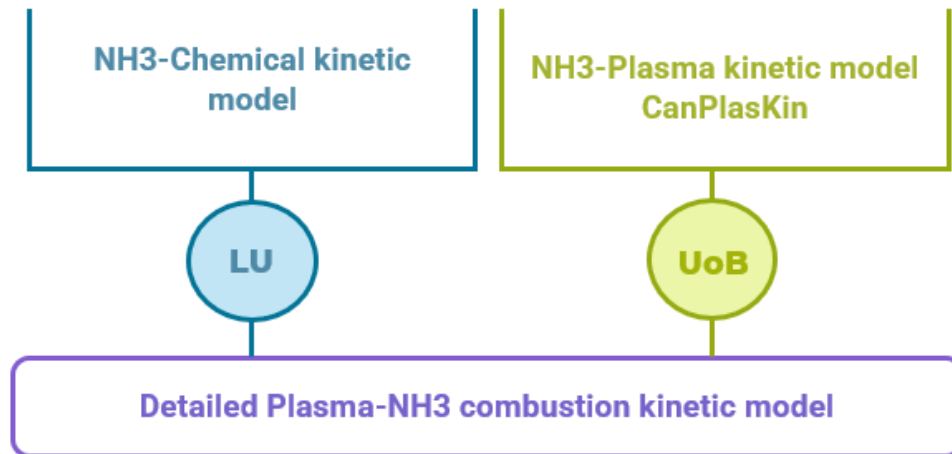


Figure 17: Schematic of the outcome achieved in CAIPIRINH3A:D2.1

The detailed plasma-NH<sub>3</sub> combustion kinetic model was developed in collaboration with two CAIPIRINH3A partners, one at Lund University (LU) and the other at the University of Birmingham (UoB). The former developed the chemical reaction during the combustion, while the latter modelled the plasma kinetics and integrated the ODEs of thermal reactions to plasma kinetics by developing a 0D C++ Cantera solver. The comprehensive plasma-NH<sub>3</sub> combustion kinetic model is divided into two main parts as shown in the above schematic,

1. Detailed, accurate chemical kinetic model development at LU
2. Plasma kinetic model and solver development at UoB

At LU, a comprehensive, accurate thermal kinetic model for NH<sub>3</sub> combustion was developed incorporating recent advances in chemiluminescence sub-mechanisms. The detailed mechanism was validated against experimental data such as ignition delay time, speciation, flame propagation speed and flame structure and other reported kinetic mechanisms from literature. Several experiments of flame structure and laminar burning velocity measurement were conducted at LU and other data are taken from reported measurements. The developed chemical kinetic model exhibits agreement with available measurements of laminar burning velocity within  $\pm 2$  cm/s, ignition delay times within  $\pm 27$ -40%, and major species concentrations in flames, including NO<sub>x</sub> within  $\pm 30\%$ .

At UoB, a 0D plasma–chemical kinetic solver, CanPlasKin, was developed based on an operator-splitting framework for plasma–combustion coupling. The solver employs a hybrid strategy combining cross-section-based and algebraic electron-temperature ( $T_e$ )-based formulations for calculating electron-impact reaction rates, significantly reducing computational cost and enabling rapid time integration for CFD coupling. A key capability of CanPlasKin is the automated generation of reaction pathways at user-specified time instances, allowing identification of dominant reaction channels and key intermediates. This facilitates mechanistic analysis of the interaction between plasma kinetics and thermal NH<sub>3</sub> oxidation chemistry, and enables quantification of the relative contributions of electron-impact and thermal pathways. The solver was validated against experimental data for plasma-assisted hydrogen oxidation in lean H<sub>2</sub>/O<sub>2</sub> mixtures and ignition delay times in diluted H<sub>2</sub>/O<sub>2</sub>/He mixtures, showing good agreement across a wide temperature range. Further validation of the reduced NH<sub>3</sub>/air/plasma mechanism is ongoing using available experimental data on plasma-assisted ignition, oxidation, and NO<sub>x</sub> formation. In parallel, UoB is developing a new reduced plasma–chemical kinetic mechanism derived from detailed coupled electron–thermal kinetic models for the NH<sub>3</sub>/air/plasma system and expected to be delivered in the coming months.

The outcomes of the deliverable are outlined as follows,

1. Developed a novel kinetic model for NH<sub>3</sub> combustion with rigorous experimental validation that resolves significant current discrepancies with experimental flame speed, ignition delay, speciation and flame structure data.
2. Developed NH<sub>3</sub>-plasma combustion solver (CanPlasKin) that integrated plasma kinetics and chemical kinetics in 0D with Cantera C++ solver for plasma-assisted NH<sub>3</sub> combustion.

The work has resulted in the successful delivery of D2.1, and disseminated the outcomes in four peer-reviewed publications and conference presentations as given below, confirming that all technical activities are on track.

- Zubairova, A., Chen, J., Konnov A.A., Brackmann, C., Flame structure study of premixed NH<sub>3</sub>/O<sub>2</sub>/Ar flames using Raman spectroscopy. *Combust. Flame*, 280: 114382 (2025).
- Han, X., Konnov A.A., Laminar Burning Velocity and Unburnt Temperature: Comparative Analysis Across a Broad Temperature Range of Atmospheric NH<sub>3</sub>+H<sub>2</sub> Flames. *Combust. Flame*, 275: 114117 (2025).
- Chen, J., Konnov A.A., When ammonia addition increases the burning velocity of a fuel blend with nitromethane. *Combust. Flame*, 277: 114230 (2025).
- Ravelid J., Sun J., Kornienko V., Konnov A.A., Kristensson E., Bao Y., Ehn A., 2D imaging of atomic oxygen reaction dynamics after a nanosecond pulse discharge using Light-field Amplitude Control. *Plasma Sources Sci. Technol*, 34: 105010 (2025).
- U. P. Padhi, M. Raveesh, C. Brackmann, J. Bood, A. A. Konnov, chemiluminescence in premixed HH<sub>3</sub>+O<sub>2</sub>+Ar flames: spatial characterization and kinetic modeling, presentation at the 41st International Symposium on Combustion, 135077115 (2026).

Zenodo links for the developed detailed kinetic mechanism for thermal and plasma-NH<sub>3</sub> combustion is provided in annex I and II, respectively.

## 5 Conclusions

Under WP2 - T2.1 (D2.1) the research on “NH<sub>3</sub> plasma-combustion kinetics and modelling” is carried out collaboratively by CAIPIRINH3A partners at LU and UoB. Within the deliverable, LU developed a detailed and accurate chemical kinetic mechanism for NH<sub>3</sub> combustion that can be used for NO<sub>x</sub> prediction and control. The mechanism was validated rigorously against fundamental combustion data such as ignition delay time, speciation, flame propagation speed and flame structure. Experimental measurements performed at LU, together with literature data, were used for validation and comparison with existing kinetic mechanisms. The model shows good agreement with measurements, predicting laminar burning velocities within  $\pm 2$  cm/s, ignition delay times within  $\pm 27$ –40%, and major species concentrations in flames within  $\pm 30\%$ . Importantly, the profiles of NO and N<sub>2</sub>O, key pollutants and greenhouse gases, are reproduced within experimental uncertainties of  $\pm 5\%$  and  $\pm 10\%$ , respectively.

At UoB, the chemical kinetic mechanism was coupled with plasma kinetics and a 0D plasma-chemical kinetic solver (CanPlasKin) was developed. The solver employs a hybrid approach combining cross-section-based and electron-temperature-based formulations for electron-impact reaction rates, enabling computationally efficient simulations suitable for CFD coupling. It also provides an automated reaction pathway generator that identifies dominant reaction channels and key intermediates governing plasma-assisted NH<sub>3</sub> oxidation. The solver was validated against reported experimental data for plasma-assisted hydrogen oxidation and ignition delay times in H<sub>2</sub>/O<sub>2</sub>/He mixtures, showing good agreement over a wide temperature range. UoB is currently undertaking further validation of the implemented reduced NH<sub>3</sub>/air/plasma mechanism against available experimental data from the literature. Further, UoB is developing a new reduced plasma-chemical kinetic mechanism that will be used for CFD-based simulations within CAIPIRINH3A.

The developed detailed kinetic mechanism for thermal NH<sub>3</sub> combustion is provided in Annex I and the first version of the NH<sub>3</sub> plasma kinetic mechanism used in CanPlasKin is provided in Annex II. By M12, D2.1 already made several important achievements, which are reflected in four scientific publications and several presentations/posters at conferences over the year. The NH<sub>3</sub> plasma-combustion kinetics model will be used to calculate fundamental combustion characteristics of ammonia/air mixture with and without plasma, and further extended across multiple tasks within different work packages. This will serve as the central kinetic framework for all subsequent modelling activities in WP2 (T2.2) and WP3 (T3.2), ensuring methodological consistency. The plasma-assisted NH<sub>3</sub> ignition model established in this work provides a robust foundation for investigating stratified mixtures, flow velocity effects, and plasma dynamics, thereby directly advancing the project toward its objective of a unified and predictive model for plasma-assisted ammonia combustion.

## 6 Annexes

### Annex I: A Detailed Chemical Kinetic Model for NH<sub>3</sub> combustion

This is a detailed chemical kinetic model for ammonia combustion developed at LU. The kinetic model consists of a reaction mechanism file (.txt) that contains 44 species and 428 reactions which include the chemiluminescence signature of various excited species in ammonia-fuelled flames. In addition, it contains a thermodynamic file (.dat) and a transport data file (.txt). The link to the kinetic model can be found in Zenodo at: <https://zenodo.org/records/19725531>

The files are compatible with any solvers line CHEMKIN, CANTERA, OPENSMOKE, FlameMaster, Zero-RK, etc.

### Annex II: NH<sub>3</sub>-Plasma Combustion Mechanisms and CanPlasKin Solver

This annex includes plasma-assisted ammonia combustion kinetic mechanisms and CanPlasKin solver framework.

#### Plasma-assisted combustion Mechanism

The thermal mechanism and plasma mechanism are integrated for plasma-assisted combustion kinetics modeling. The mechanism files are provided in YAML format which is supported by CANTERA.

Original YAML mechanism from literature<sup>16</sup> can be found at: <https://zenodo.org/records/19816645>

Refined YAML mechanism can be found at: <https://zenodo.org/records/19818598>

#### CanPlasKin Solver

This is a custom-developed plasma reaction rate solver implemented in C++ within the Cantera framework. The solver introduces a log-polynomial formulation for electron-impact reaction rates, specifically designed for non-equilibrium plasma conditions relevant to ammonia combustion. The solver enables accurate evaluation of plasma reaction rates as a function of electron temperature, incorporating logarithmic and inverse temperature dependencies. It supports integration into zero-dimensional, one-dimensional, and CFD-based plasma simulations. The main files and header files are provided in Zenodo at:

<https://zenodo.org/records/19818944>

<https://zenodo.org/records/19819448>

<https://zenodo.org/records/19819604>

<https://zenodo.org/records/19819760>