

Non-Thermal Plasma Modelling in Novel Multiphase Reactor Systems

50%

Of worlds food production
relies on ammonia-
derived fertilisers

\$80bn

Global Market Value

~2%

Global CO2 emissions

2nd

Most produced chemical
globally

90%

Of Global Ammonia
Produced by the
Haber-Bosch process

Introduction

Haber-Bosch problem

- Highly energy-intensive: stable N₂ and CH₄.
- E demand: H₂ - SMR (~80%), NH₃ synthesis (~20%)
- N≡N triple bond is the rate-determining step.

Non-thermal plasma (NTP)

- Energetic e activate N₂.
- Enables NH₃ synthesis at low T & P conditions.
- DBD reactors promising: remain limited by plasma scalability and energy cost.

Emerging sustainable alternatives

- Multiple routes under development: electrolysis-based H₂, electrochemical N₂ reduction.
- Plasma catalysis for: CO₂ dissociation, CH₄ activation, NH₃ synthesis.
- Tribo-plasma fluidised beds
- Alternative NTP generation: contact electrification --> triboelectric discharges.

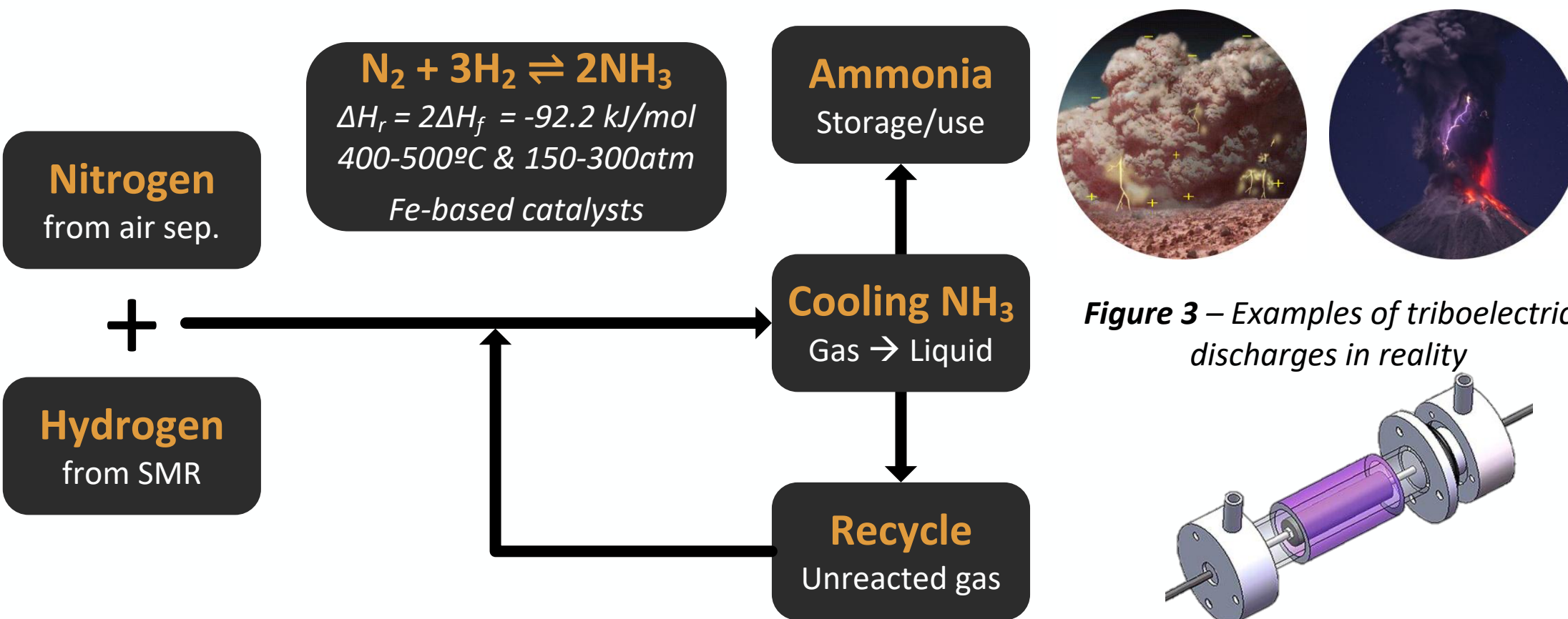


Figure 1 – Simple representation of Haber-Bosch process steps

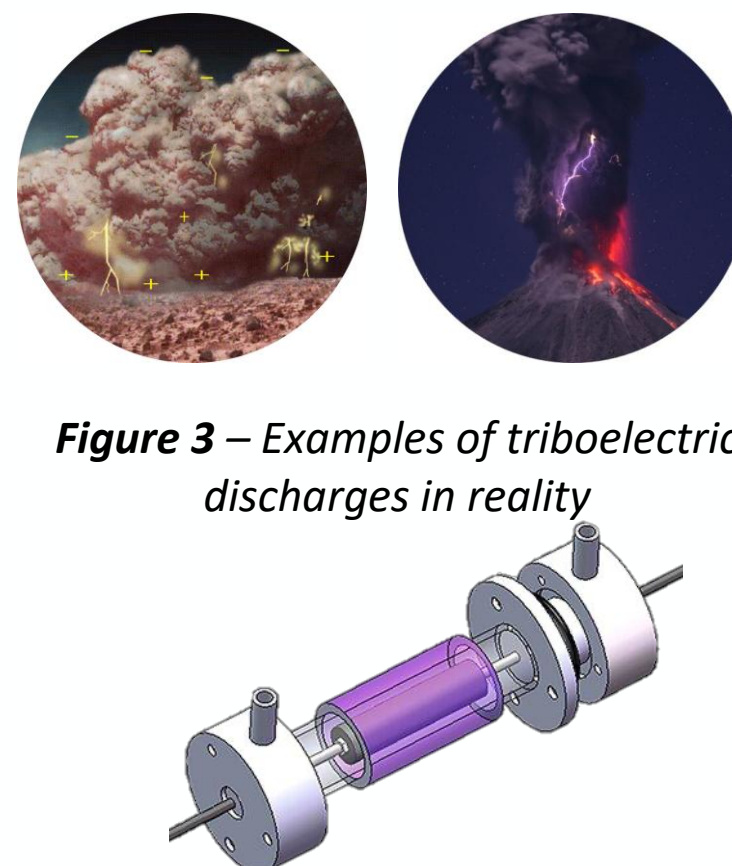


Figure 3 – Examples of triboelectric discharges in reality

Figure 2 – Schematic of a Dielectric Barrier Discharge reactor

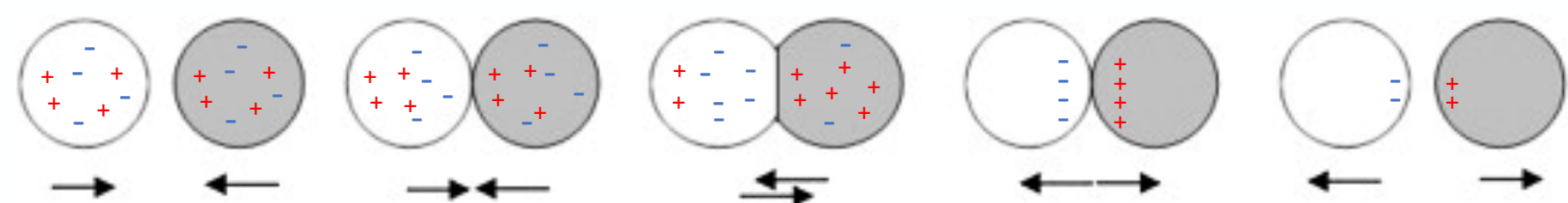
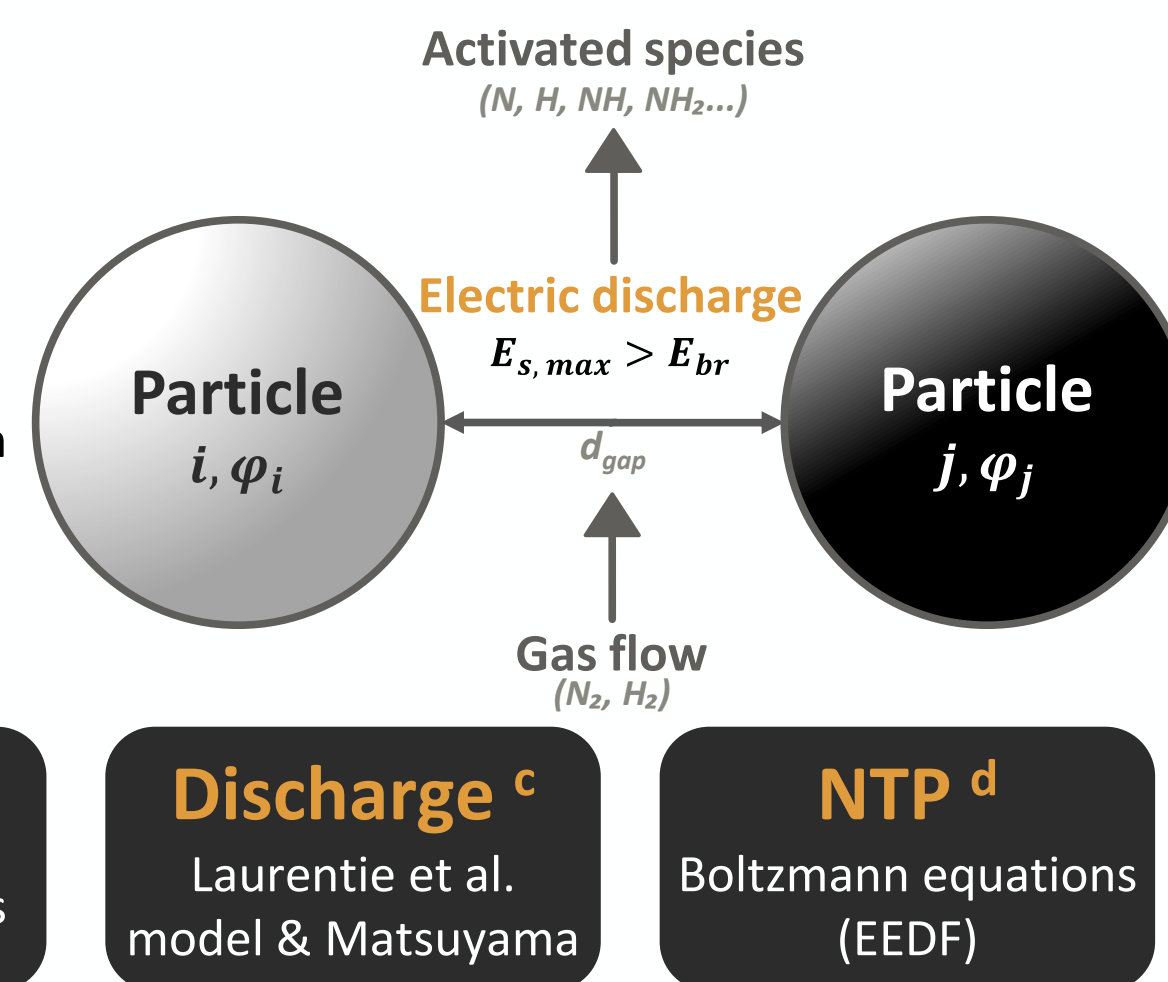


Figure 4 – Stepwise visualisation of the charge evolution during the collision between two particles, each particle has a different work functions (Adapted from Laurentie et al. (2003))

Aims & Objectives

To develop a computationally tractable model to assess the feasibility of gas-solid-plasma fluidised bed reactors.

- Couple fluid-particle hydrodynamics, contact charging, and plasma kinetics within a single continuum modelling framework.
- Decouple fast plasma kinetics from slow reactor dynamics



Modelling Framework

Each phase is described by its governing physics within a continuum framework. Particle and electron dynamics are captured statistically, while the gas phase is resolved through conservation equations. Shared source terms then interlink the phases, coupling flow, charging, and chemistry.

$$\frac{3}{2} \frac{\partial}{\partial t} \left(\alpha_{pi} \rho_{pi} \frac{\Theta_{pi}}{m_{pi}} \right) + \frac{3}{2} \nabla \cdot \left(\alpha_{pi} \rho_{pi} \mathbf{U}_{pi} \frac{\Theta_{pi}}{m_{pi}} \right) = \sum_{h=i,j} \left(\underbrace{-\nabla \cdot \mathbf{q}_{ih}}_{\text{Collisional flux}} + \underbrace{\gamma_{ih}}_{\text{Collisional source}} \right) \quad (a_1)$$

$$\frac{\partial}{\partial t} \left(\frac{\alpha_{pi} \rho_{pi} Q_{pi}}{m_{pi}} \right) + \nabla \cdot \left(\frac{\alpha_{pi} \rho_{pi} Q_{pi} \mathbf{U}_{pi}}{m_{pi}} \right) = \sum_{h=i,j} \left(\underbrace{-\nabla \cdot \theta_{ih}^q(q_{pi})}_{\text{Collisional charge flux}} + \underbrace{X_{ih}^q(q_{pi})}_{\text{Collisional charge source}} \right) \quad (a_2)$$

$$\frac{\partial (\rho c_p T_{gas})}{\partial t} + \nabla \cdot (\rho u c_p T_{gas}) = \underbrace{\nabla \cdot (k \nabla T_{gas})}_{\text{Thermal diffusion}} - \sum_{k=1}^N \underbrace{\dot{\omega}_k h_k W_k}_{\text{Heat of reaction}} + \underbrace{\dot{E}_p}_{\text{Plasma heating}} + \underbrace{\sum_k (-\dot{E}_{vib}^k + \dot{R}_{VT}^k)}_{\text{Vibrational-translational exchange}} \quad (b)$$

$$\nabla^2 \phi = -\frac{\rho q}{\epsilon} \quad (c) \quad \frac{\partial f_e}{\partial t} + \nabla \cdot (c_e f_e) + \frac{\partial}{\partial c_e} \cdot \left(\frac{q_e \mathbf{E} f_e}{m_e} \right) = \left(\frac{\partial f_e}{\partial t} \right)_{\text{coll}} \quad (d_1) \quad \frac{\partial n_e}{\partial t} + \nabla \cdot \Gamma_e = S_e \quad (d_2)$$

$$\mathbf{E} = -\nabla \phi$$

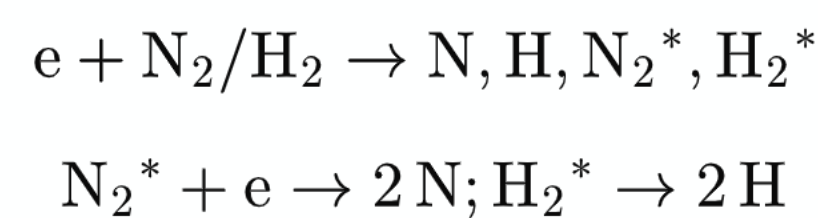
Conclusions

- Proof-of-concept 0D model; successfully coupled all phases for NH₃ synthesis.
- Triboelectric discharges sustain electron energies; sufficient to activate N₂ and H₂.
- NH₃ produced but conversion low.
- Vibrational excitation dominates at low E/N.
- Establishes a validated kinetics framework as the foundation for future sims.

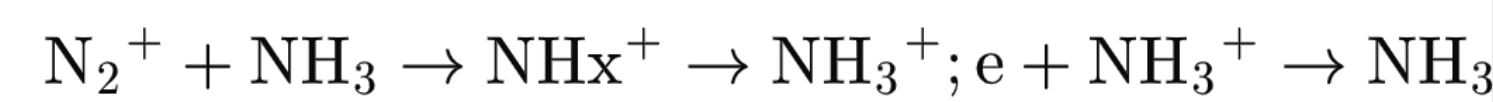
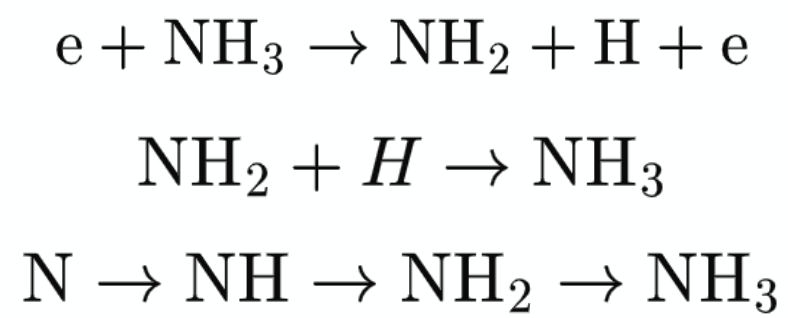
Modelling Challenges

- A multi-timescale multi-physical problem
- Developing a computationally efficient model that accurately captures the physics
- Validation of model is challenging due to limited experimental work
- Time of PhD to validate experimentally

Gas Ionisation:



Reaction Mechanisms:



Results & Validation

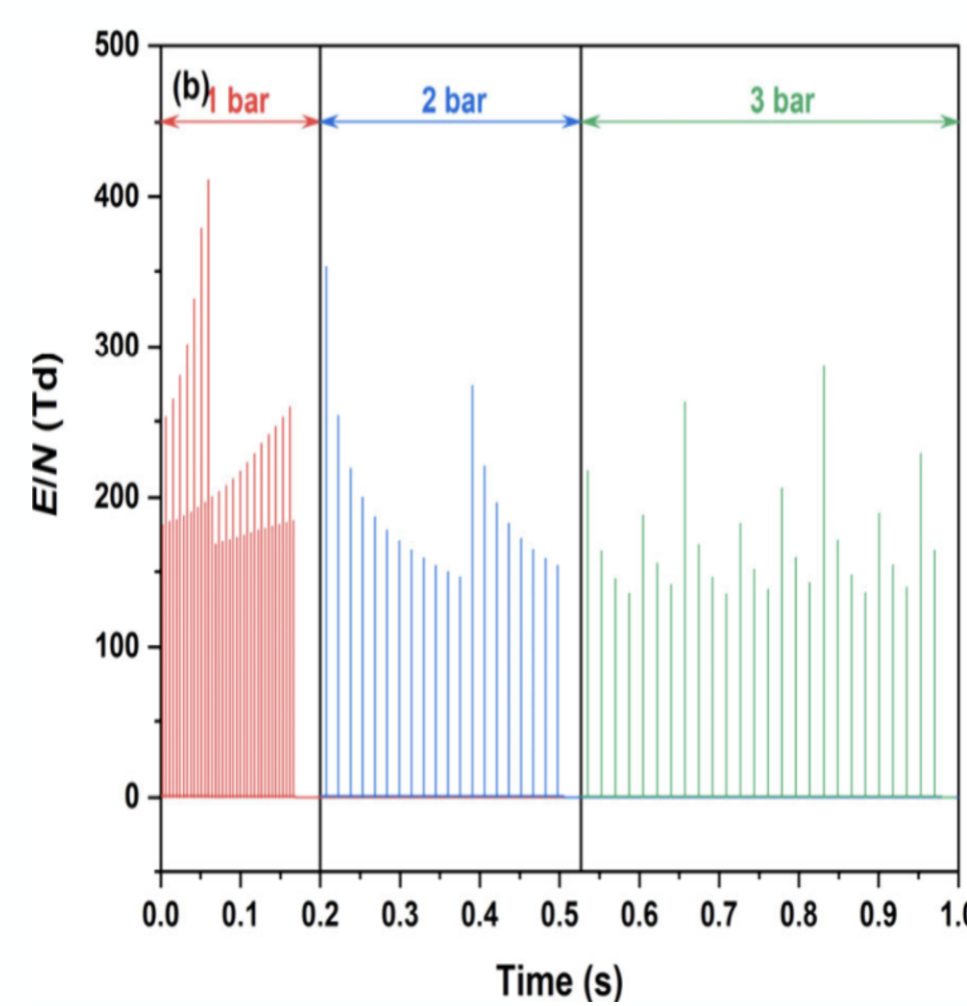


Figure 5 – Validation of the local electric field in the simulation model to experimental data

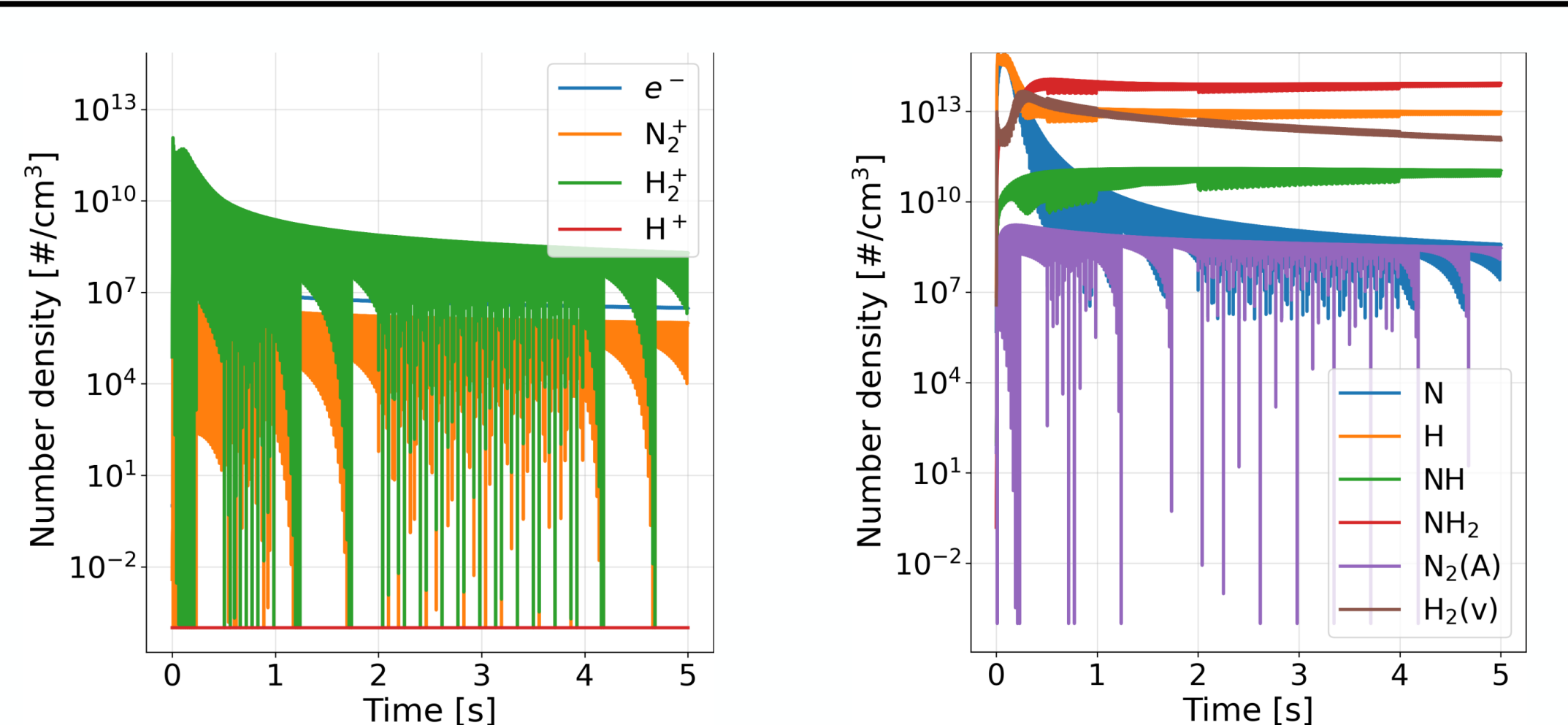
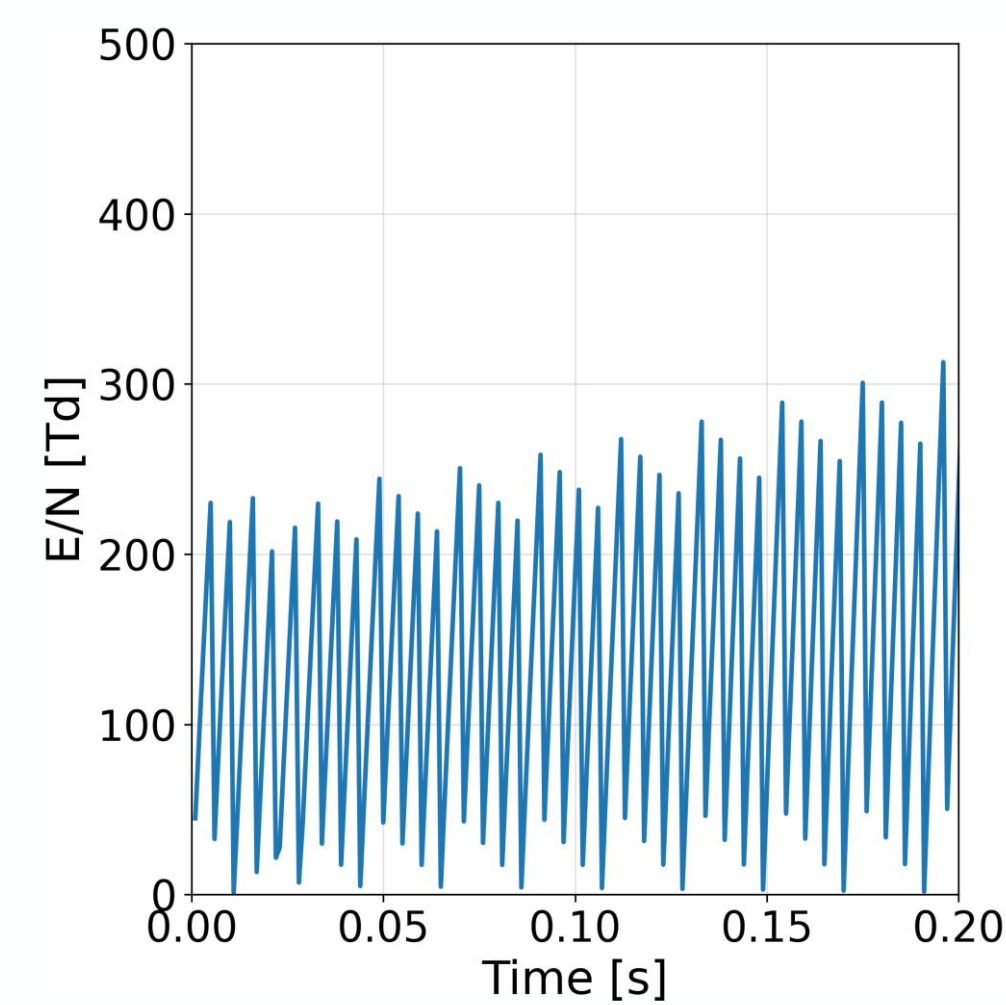


Figure 6 – Simulations results showing successful generation of non-thermal plasma intermediate species and subsequently the consumption of feedstocks and the generation of precursors for ammonia production

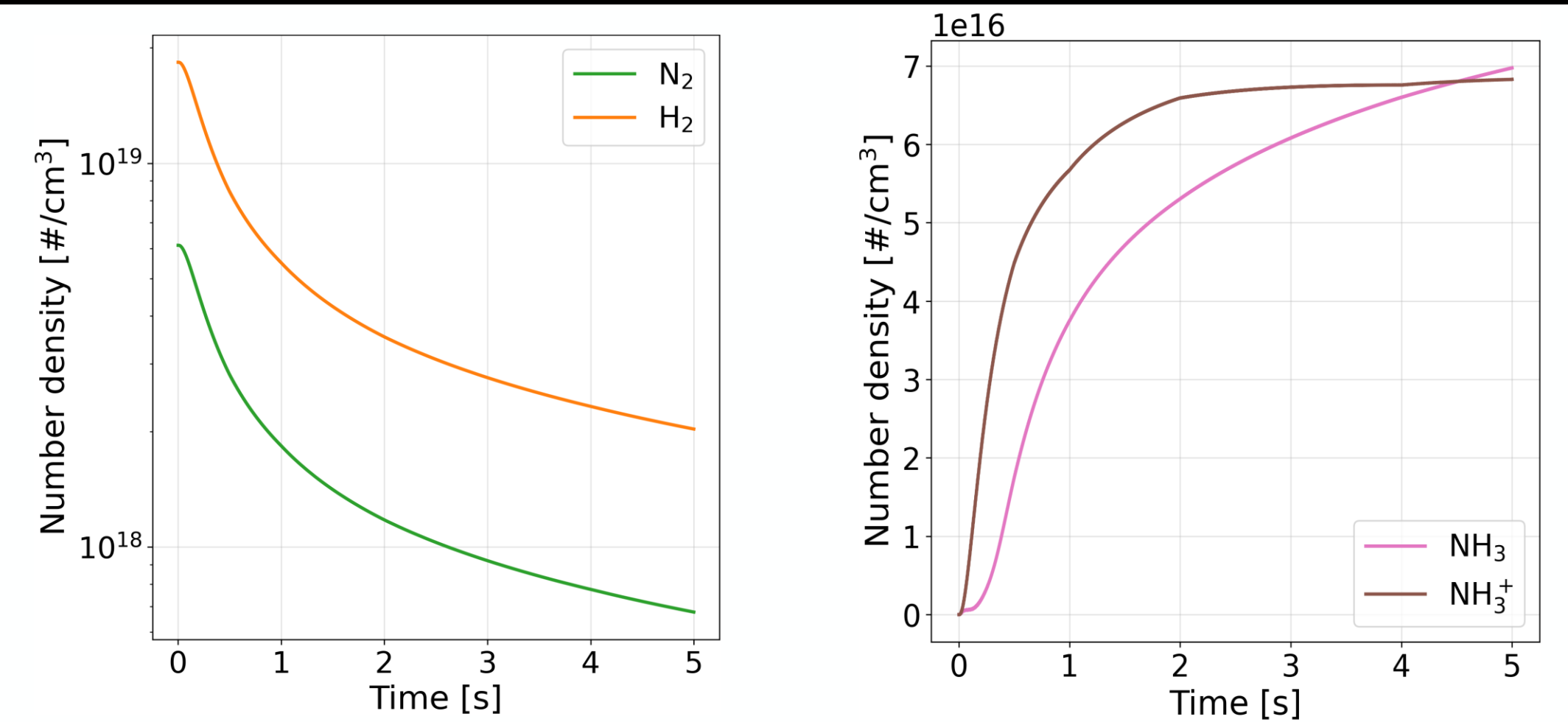


Figure 7 – Graphs highlighting the consumption of feedstock and generation of desired product (Ammonia)

Future Work

- Refine 0D chemistry and validated 3D hydrodynamic solver.
- Fully coupled 3D reactive fluidised bed model.
- Parametric design study: particle material, size, fluidisation behaviour, reaction.
- Sensitivity analysis and calibration of uncertain model parameters.
- Catalyst screening, experimental validation, TEA.