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Predictive modeling of warm plasmas: from understanding chemistry to optimizing reactor design for H₂ synthesis

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Predictive modeling of warm plasmas: from understanding chemistry to optimizing reactor design for H₂ synthesis

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Summary

The industrial transition towards H_2 as both a reactant and an energy carrier has led to a rapidly increasing demand. Although H_2 is often described as a carbon-free fuel, this is only valid when it is produced without associated CO_2 emissions. Currently, H_2 is primarily generated via steam methane reforming, which results in approximately 13 kg of CO_2 emissions per kg of H_2 produced. Consequently, alternative production pathways must be explored to achieve truly carbon-free H_2 .

Plasma ((partially) ionized gas) has emerged as a promising medium for gas-phase chemistry. Its high-energy environment enables reaction pathways that are inaccessible under conventional conditions. However, warm plasmas typically reach temperatures of several thousand Kelvin, making some experimental diagnostics challenging.

As a result, our understanding of plasma processes relies heavily on modeling. By incorporating the relevant physical and chemical phenomena into advanced numerical simulations, plasma behavior can be studied in detail, revealing the mechanisms that drive desired reactions. When sufficiently accurate, such models also enable the optimization of reactor conditions and design, leading to improved conversion efficiencies, reduced energy consumption, and enhanced product selectivity.

This work aims to develop plasma models from first principles, without reliance on experimental input, and able to reproduce observed experimental results. These predictive models provide insight into complex plasma chemistry, and they support experimental research by offering guidance, not only on reaction pathways but also on gas flow dynamics and heat transfer.

A comprehensive introduction to the underlying concepts is provided in Chapter 1, where a clear distinction is made between global models, which focus on detailed plasma kinetics, and multidimensional models, which additionally incorporate gas flow and heat transfer. Chapter 2 presents the governing equations used throughout this work for both modeling approaches.

In Chapter 3, the first multidimensional plasma model with an extensive chemistry set is introduced. The results demonstrate significant differences compared to global models of the same system, highlighting the importance of spatial effects in warm plasmas. While this chapter represents an important step towards predictive multidimensional

modeling, further refinement is required to improve agreement with experimental observations.

Global modeling is employed in Chapter 4 to explore optimal operating conditions for plasma-based NH_3 conversion. Continuous warm plasma operation is found to yield the lowest energy cost, in agreement with experimental data. Additionally, the model predicts that preheating the feed gas reduces energy consumption in pulsed plasma systems and identifies plasma-assisted NH_3 cracking as a promising direction for future experimental investigation.

Multidimensional models in Chapters 5 and 7 achieve improved agreement with experiments for warm NH_3 and CH_4 plasmas, respectively. These models provide insight into multidimensional physical effects, such as the detrimental impact of turbulent transport in NH_3 plasmas, and they allow initial recommendations for reactor design improvements.

In Chapter 6, a two-zone global model is developed to study nanosecond pulsed CH_4 plasmas. By self-consistently calculating gas temperatures, the model reduces the need for user-defined inputs, while maintaining good agreement with experimental results. This approach enables detailed analysis of chemical pathways in both the plasma region and the surrounding colder gas, highlighting preheating as a strategy for reducing energy costs in CH_4 reforming.

In conclusion, this thesis advances predictive plasma modeling in both global and multidimensional frameworks. These tools pave the way for the computational design and optimization of plasma reactors prior to experimental implementation, significantly reducing development time and cost.

Samenvatting

De industriële transitie naar H_2 als zowel grondstof als energiedrager heeft geleid tot een snel toenemende vraag. Hoewel H_2 vaak wordt omschreven als een koolstofvrije brandstof, is dit enkel correct wanneer het wordt geproduceerd zonder bijbehorende CO_2 -uitstoot. Momenteel wordt H_2 voornamelijk geproduceerd via stoomreforming van methaan, wat resulteert in ongeveer 13 kg CO_2 -uitstoot per kg geproduceerde H_2 . Daarom moeten alternatieve productieroutes worden onderzocht om werkelijk koolstofvrije H_2 te verkrijgen.

Plasma ((partieel) geïoniseerd gas) is een veelbelovend medium voor gasfasechemie. De hoogenergetische omgeving maakt reactiepaden mogelijk die onder conventionele omstandigheden niet toegankelijk zijn. Warm plasma bereikt echter typisch temperaturen van enkele duizenden Kelvin, wat experimentele diagnostiek soms uitdagend maakt.

Als gevolg hiervan steunt ons begrip van plasmaprocessen sterk op modellering. Door relevante fysische en chemische fenomenen te integreren in geavanceerde numerieke simulaties, kan het gedrag van plasma in detail worden bestudeerd en kunnen de mechanismen achter gewenste reacties worden blootgelegd. Als ze voldoende nauwkeurig zijn, maken dergelijke modellen ook de optimalisatie van reactorcondities en -ontwerp mogelijk, wat leidt tot hogere conversies, lager energieverbruik en verbeterde productselectiviteit.

Dit werk heeft tot doel plasmamodellen te ontwikkelen vanaf eerste principes, zonder afhankelijkheid van experimentele input, terwijl waargenomen experimentele resultaten toch worden gereproduceerd. Deze voorspellende modellen bieden inzicht in complexe plasmachemie en ondersteunen experimenteel onderzoek, door niet alleen informatie te verschaffen over reactiemechanismen, maar ook over gasstromingsdynamica en warmtetransport.

Een uitgebreide inleiding tot de onderliggende concepten wordt gegeven in Hoofdstuk 1, waar een duidelijk onderscheid wordt gemaakt tussen globale modellen, die zich richten op gedetailleerde plasmakinetiek, en multidimensionale modellen, die daarnaast ook gasstroming en warmtetransport omvatten. Hoofdstuk 2 presenteert de vergelijkingen die in dit werk voor beide types modellering worden gebruikt.

In Hoofdstuk 3 wordt het eerste multidimensionale plasmamodel met een uitgebreid chemische set geïntroduceerd. De resultaten tonen significante verschillen ten opzichte van globale modellen van hetzelfde systeem, wat het belang van ruimtelijke effecten in warm plasma benadrukt. Hoewel dit hoofdstuk een belangrijke stap vormt voor voorspellende multidimensionale modellering, is verdere verfijning noodzakelijk om een betere overeenstemming met experimentele waarnemingen te bereiken.

In Hoofdstuk 4 wordt globale modellering toegepast om optimale condities voor plasma-gebaseerde NH_3 -conversie te onderzoeken. Continue werking van warm plasma blijkt de laagste energiekost op te leveren, in overeenstemming met experimentele data. Daarnaast voorspelt het model dat voorverwarming van het invoergas het energieverbruik in gepulste plasmasystemen verlaagt, waardoor plasma-geïnitieerd NH_3 -kraken mogelijk veelbelovend is voor toekomstig experimenteel onderzoek.

De multidimensionale modellen in Hoofdstukken 5 en 7 tonen een verbeterde overeenstemming met experimenten voor respectievelijk warme NH_3 - en CH_4 -plasma's. Deze modellen verschaffen inzicht in multidimensionale fysische effecten, zoals de nadelige invloed van turbulente transportprocessen in NH_3 -plasma's, en maken eerste aanbevelingen mogelijk voor verbeteringen in het reactorontwerp.

In Hoofdstuk 6 wordt een twee-zone globaal model ontwikkeld voor de studie van nanoseconde-gepulste CH_4 -plasma's. Door de gastemperatuur zelfconsistent te berekenen, wordt de nood aan experimentele input verminderd, terwijl een goede overeenstemming met experimentele resultaten behouden blijft. Deze aanpak maakt een gedetailleerde analyse mogelijk van chemische reactiepaden, zowel in het plasma als in het omringende koudere gas, waarbij voorverwarming opnieuw naar voren komt als een strategie om de energiekost van CH_4 -conversie te verlagen.

Algemeen levert dit proefschrift belangrijke vooruitgang in de ontwikkeling van voorspellende plasmamodellen binnen zowel globale als multidimensionale kaders. Deze modellen maken het mogelijk om plasmareactoren computationeel te ontwerpen en te optimaliseren vóór experimentele implementatie, wat de ontwikkelingstijd en -kosten aanzienlijk vermindert.

Résumé

La transition industrielle vers l'hydrogène (H_2) en tant que réactif et vecteur d'énergie a entraîné une augmentation rapide de sa demande. Bien que H_2 soit souvent décrit comme un carburant décarboné, cela n'est valable que s'il est produit sans émissions de CO_2 . Actuellement, H_2 est principalement synthétisé par vaporeformage du méthane, ce qui génère environ 13 kg de CO_2 par kg de H_2 produit. Il est donc nécessaire d'explorer des voies de production alternatives afin d'obtenir un hydrogène décarboné.

Le plasma (gaz ionisé) s'est imposé comme un milieu prometteur pour la chimie en phase gazeuse. Son environnement hautement énergétique permet d'accéder à des voies réactionnelles inaccessibles dans des conditions conventionnelles. Cependant, les plasmas dits « chauds » atteignent généralement des températures de plusieurs milliers de Kelvin, rendant les diagnostics expérimentaux difficiles.

Par conséquent, la compréhension des processus du plasma repose beaucoup sur la modélisation. En intégrant les phénomènes physiques et chimiques dans des simulations numériques, il est possible d'étudier le comportement du plasma et de mettre en évidence les mécanismes des réactions. Avec une précision suffisante, ces modèles permettent aussi d'optimiser les conditions de fonctionnement des réacteurs, conduisant à de meilleures conversions, une consommation énergétique réduite et une sélectivité accrue.

Ce travail vise à développer des modèles de plasma à partir des principes fondamentaux, sans recours direct aux données expérimentales, tout en reproduisant les résultats observés. Ces modèles prédictifs offrent une meilleure compréhension de la chimie des plasmas et soutiennent les recherches expérimentales en permettant de mieux comprendre les mécanismes réactionnels, ainsi que les phénomènes d'écoulement et de transfert thermique.

Une introduction aux concepts fondamentaux est présentée au Chapitre 1, avec une distinction entre les modèles globaux et multidimensionnels, qui intègrent l'écoulement des gaz et le transfert thermique. Le Chapitre 2 présente les équations gouvernantes utilisées pour ces deux approches.

Au Chapitre 3, le premier modèle multidimensionnel intégrant un mécanisme chimique étendu est détaillé. Les résultats mettent en évidence des différences significatives par rapport aux modèles globaux, soulignant l'importance des effets spatiaux dans les plasmas chauds. Bien que ce chapitre constitue une étape importante, des améliorations sont nécessaires pour mieux reproduire les observations expérimentales.

La modélisation globale est utilisée au Chapitre 4 pour explorer les conditions optimales de conversion de NH_3 assistée par plasma. Le fonctionnement continu en plasma chaud présente le coût énergétique le plus faible, en accord avec les données expérimentales. De plus, le modèle prédit que le préchauffage du gaz d'alimentation réduit la consommation énergétique dans les systèmes plasma pulsés, identifiant le craquage de NH_3 initié par plasma comme une piste prometteuse.

Les Chapitres 5 et 7 montrent une meilleure concordance avec les expériences pour des plasmas chauds de NH_3 et de CH_4 , respectivement. Ces modèles permettent de mieux comprendre les effets physiques multidimensionnels, tels que l'impact du transport turbulent dans les plasmas de NH_3 , et ouvrent la voie à des recommandations pour la conception des réacteurs.

Au Chapitre 6, un modèle global à deux zones est développé pour étudier les plasmas pulsés de CH_4 à l'échelle nanoseconde. En calculant la température du gaz de manière auto-cohérente, le modèle réduit la nécessité d'entrées définies par l'utilisateur tout en conservant une bonne concordance avec les résultats expérimentaux. Cette approche permet une analyse détaillée des voies réactionnelles dans le plasma et dans le gaz environnant, plus froid, mettant en évidence le préchauffage comme stratégie de réduction des coûts énergétiques du reformage du CH_4 .

En conclusion, cette thèse apporte des avancées significatives dans le développement de modèles prédictifs de plasma, tant dans des cadres globaux que multidimensionnels. Ces outils ouvrent la voie à la conception et à l'optimisation des réacteurs plasma avant leur mise en œuvre expérimentale, réduisant considérablement le temps et les coûts de développement.

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The median self-published book is read by only a few dozen people. While I doubt this thesis will be read front-to-back by anyone except my jury members and promoters, I do think this page will be opened and read a few dozen times, or scanned for a name, whatever floats your boat. In my opinion, it is what defines the thesis. A PhD is rarely a successful endeavor on your own. Therefore, these pages thank the people who helped shape the last four years and every single page of this book.

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Table of contents

Introduction	17
1.1 An introduction to hydrogen gas.....	19
1.2 An introduction to plasma.....	20
1.3 An introduction to modeling	21
1.4 The hydrogen rainbow.....	22
1.5 Plasma pathways towards H ₂	23
1.5.1 Methane reforming	24
1.5.2 Dry reforming of methane.....	25
1.5.3 NH ₃ cracking.....	25
1.6 Thermal chemistry vs electron-impact reactions in warm plasma	26
1.7 State-of-the-art on plasma modeling	30
1.7.1 Multidimensional CFD modeling for warm plasmas.....	30
1.7.2 Global chemical kinetics modeling	31
1.8 Aim of this thesis	32
General Methodology	35
2.1 Thermal chemical kinetics	37
2.1.1 Rate coefficients	37
2.2 Detailed balancing	38
2.3 Chemistry reduction	39
2.4 Multidimensional CFD models.....	42
2.4.1 3D flow models	44
2.4.2 Translation to 2D axisymmetric models.....	44
2.4.3 Fluid flow equations	45
2.4.4 Current conservation equations	47
2.4.5 Heat transfer equations	48
2.4.6 Gas property equations	48

2.4.7	Transport of species equations.....	50
2.5	Global models.....	51
2.5.1	General global modeling equations	52
2.5.2	Heat balance equations to calculate EC	53
2.5.3	Two-zone model description	54
2.5.4	Global plasma model equations.....	56
2.5.5	Global cold model equations.....	57
2.5.6	Energy and mass exchange equations between zones	59
2.5.7	Advantages and limitations of the two-zone approach.....	62
	Multidimensional model of dry reforming of methane with oxygen addition in an atmospheric pressure glow discharge	65
3.1	Introduction.....	67
3.2	Computational and experimental details.....	68
3.2.1	3D geometry and meshing	69
3.2.2	2D inlet gas velocity profile	69
3.2.3	2D geometry and boundary conditions.....	70
3.2.4	Experimental setup and gas composition	74
3.3	Results and discussion.....	76
3.3.1	Chemistry reduction	76
3.3.2	3D RANS SST flow model.....	78
3.3.3	Comparison of 2D model and experimental results.....	80
3.3.4	Temperature and thermodynamic analysis.....	83
3.3.5	Plasma species analysis	86
3.3.6	Heat balance analysis	90
3.3.7	Afterglow analysis.....	92
3.3.8	Importance of diffusive and convective fluxes	95
3.3.9	Reaction pathway analysis.....	97
3.4	Conclusion	100

Performance insights into plasma-based NH₃ cracking from a global model	103
4.1 Introduction	105
4.2 Computational details	106
4.2.1 Operating conditions of warm plasmas	106
4.2.2 Reaction mechanism.....	108
4.2.3 Performance metrics	110
4.2.4 Validation of the model	111
4.3 Results and discussion	113
4.3.1 NH ₃ conversion	114
4.3.2 Final product composition	117
4.3.3 Time to reach full conversion	119
4.3.4 Underlying chemistry governing the NH ₃ conversion.....	120
4.3.5 EC of NH ₃ cracking at typical operating conditions.....	124
4.3.6 EC of NH ₃ conversion at constant gas temperatures	126
4.3.7 Optimization strategies for EC improvement.....	128
4.4 Conclusion	134
Multidimensional modeling of NH₃ cracking to understand turbulent effects.....	137
5.1 Introduction	139
5.2 Computational details	139
5.2.1 Reactor schematic	140
5.2.2 Geometry and boundaries.....	142
5.2.3 Turbulent transport modifier.....	147
5.2.4 Chemistry set	148
5.2.5 Performance metrics	149
5.3 Results and discussion	150
5.3.1 Chemical reduction results	150
5.3.2 Experimental validation of the model	152
5.3.3 Reaction pathway analysis in a pin-to-pin arc plasma reactor	154

5.3.4	3D modeling results.....	157
5.3.5	Effect of turbulence on conversion and energy cost	159
5.3.6	Spatial temperature and NH ₃ profiles	161
5.3.7	Changes in conversion and EC in the afterglow.....	162
5.3.8	Future reactor design from modeling insights	167
5.4	Conclusion	168
Two-zone global model of a CH₄ nanosecond pulsed plasma.....		169
6.1	Introduction.....	171
6.2	Computational details	174
6.2.1	Inferred spatial dimensions	174
6.2.2	Calculations of product selectivities.....	175
6.2.3	Chemistry set.....	175
6.3	Results and discussion.....	176
6.3.1	Key variables as a function of time.....	176
6.3.2	Product selectivities for model validation	179
6.3.3	Chemical pathway analysis.....	181
6.3.4	Suggested improvements based on modeling insights	186
6.4	Conclusion	190
Understanding soot formation in a rotating gliding arc plasma via multidimensional modeling.....		193
7.1	Introduction.....	195
7.2	Computational details	195
7.2.1	Major mixture-averaged diffusion.....	195
7.2.2	Geometry and boundary conditions	196
7.2.3	Chemistry set.....	200
7.3	Results and discussion.....	202
7.3.1	Model validation.....	203
7.3.2	Changes in flow dynamics	204

7.3.3	Localization of soot formation	206
7.4	Conclusion	209
General conclusions and outlook		211
8.1	Conclusions.....	213
8.2	Outlook	215

Chapter 1

Introduction

1.1 An introduction to hydrogen gas

The discovery of hydrogen gas (H_2) as a discrete substance is often attributed to Henry Cavendish. In 1766, he published a series of experiments in which he produced “flammable air” by dissolving iron, zinc, and tin in sulfuric acid [1]. He found that the density of “common air” was 10.8 times that of the produced “inflammable air”, close to the actual air/ H_2 density ratio of 13.6. Later, Cavendish found water to be the only product resulting in the burning of “flammable air” with oxygen, concluding that water must consist only of hydrogen and oxygen [2].

Since ammonia (NH_3) had not been isolated and thus not tested as a fuel, H_2 was the only fuel found not to produce CO_2 and any soot-like compounds arising from burning carbon-containing fuels [3]. While this lack of CO_2 formation during combustion was not interesting at the time, carbon-free fuels are more important than ever today, as CO_2 concentrations in our atmosphere are projected to reach 450 ppm by mid-century [4].

At that time, coal was used as the fuel for the industrial revolution, followed later, at the beginning of the 20th century, by oil [5]. While fossil fuels have brought us far, rising CO_2 concentrations underscore the need for a carbon-free fuel, bringing us back to H_2 .

The H_2 economy has been researched and developed for a long time, with key strides made in H_2 transport and the efficient use of H_2 as a fuel and as a reactant in chemical processes [6,7]. Today, H_2 is already a very present staple in industry, being essential as a fuel, for metallurgy, and, most importantly, as a chemical reagent, for instance, in oil refining, NH_3 production, or methanol ($MeOH$) production [7]. Evidently, these processes require a large amount of H_2 .

Currently, most H_2 is produced from fossil fuels, via steam methane reforming (SMR). However, this method also emits 13 kg CO_2 per kg H_2 when no additional carbon capture technologies are in place [8]. Carbon capture techniques reduce emissions to an average of 7 kg CO_2 per kg H_2 . Thus, while burning H_2 as fuel might not produce CO_2 , a large amount of CO_2 is produced during H_2 formation. Therefore, alternative technologies to produce H_2 without CO_2 emissions should be investigated.

Water electrolysis can be a promising alternative to SMR. The lower limit of the energy cost (EC) is the enthalpy of formation of H_2O , being -285.83 kJ/mol [8]. Current commercial water-splitting operates at an EC of 192 MJ/kg(H_2) or 387 kJ/mol(H_2), corresponding to an efficiency of 73.9 % [8]. This method requires a large amount of electrical power to be efficient and is currently only viable at a small and medium scale.

However, large scale electrolysis plants based fully on solar and wind energy are being built, like the NEOM project in Saudi Arabia, which is set to produce 650 tons of H_2 per day when fully operational [9,10]. However, there exist also other sustainable H_2 production methods, besides H_2O electrolysis. Specifically, this thesis focuses on H_2 production from other H-carrying molecules, such as NH_3 and CH_4 , for both transport and industrial utilization without emitting CO_2 .

1.2 An introduction to plasma

In 1928, Irving Langmuir coined the term plasma to describe an ionized gas with an equal number of electrons and ions so that the resulting space charge is very small [11]. This definition already encapsulates two of the three main properties of plasma: a (partially) ionized gas and quasi-neutrality. The third property is a collective behavior, as the plasma density is generally low enough that it follows Maxwell-Boltzmann statistics rather than Bose-Einstein or Fermi-Dirac statistics [12].

While the above definition is the more satisfying one, plasma is often referred to as “the fourth state of matter”. Long before Langmuir defined plasma, Faraday had already speculated on plasma in 1816 as the “fourth state of matter” and dubbed it “radiant matter” [13]. Indeed, adding energy to any gas will eventually result in partial ionization via high-energy collisions between neutral species that release electrons and form ions, creating a thermal plasma.

Langmuir’s definition of a plasma is preferred because plasma does not have to be thermal. Plasmas on Earth (e.g., neon lights) are created by applying an electric field. This electric field is applied between a positively charged electrode (anode) and a negatively charged electrode (cathode), with a gas in between them. This electric field accelerates electrons in the gas, enabling highly energetic collisions with heavier species. These collisions can be ionization collisions, creating more electrons and ions, excitation collisions, creating energetically excited states, dissociation collisions, creating radicals, or elastic collisions, heating the gas. The plasma can be sustained without heating the gas, to temperatures at which heavy-species collisions must ionize. While still a plasma, a lower gas temperature than in thermal plasmas classifies it as non-thermal, or cold plasma [14–16].

The transition from non-thermal to thermal plasma as gas temperature increases is not discrete. An intermediary region is defined as warm plasma. Here, the electrons are still accelerated by the applied electric field, but ionization can occur via electron-impact

reactions and collisions of heavy species. The gas temperature in warm plasmas reaches a few thousand Kelvin, while the electron temperature is still higher, around a few electron volts, or a few 10,000 K [17]. While this means that non-equilibrium electron chemistry can play a role, it does not mean it will significantly affect the overall chemical process, as the gas temperature is high enough for thermal processes to occur on the same timescale.

In all cases, the plasma consists of a reactive cocktail of chemical species, namely electrons, ions, and neutrals, including radicals, but also excited species with various levels of electronic, vibrational, or rotational excitation. This mix, combined with local gas heating from reactions of all the aforementioned species, enables interesting and unconventional chemical reactions [14–16].

Finally, the energy deposited in the plasma is electrical. This, in combination with the fast operating time of plasma (a quick on-off switch), makes it very compatible with fluctuating, renewable energy. This makes plasma technology an ideal candidate for the electrification of chemical reactions, such as the production of H_2 [14–16].

1.3 An introduction to modeling

The need for models and computer simulations predates the computers themselves. They are a substitute for systems in which simple analytical solutions are not possible. As such, computer simulations, as we know them today, emerged alongside the evolution of computers themselves [18].

The first actual simulation is widely considered to be a Monte Carlo simulation of neutron paths to determine scattering events, absorption, and fission. This was done in the late 1940's in the Los Alamos National Laboratory in the wake of World War II [19,20]. As is often the case, this pioneering work was done for weapon design, in this instance by increasing the understanding of fissile material.

Later, the first hydrodynamic calculations were pioneered by researchers at Los Alamos, who developed and published a particle-in-cell method for fluid flow in 1957 [21]. This leads to the computational fluid dynamics (CFD) we know today: a deterministic system solving the discretized Navier-Stokes equation for any fluid in any well-defined geometry, following any of the developed discretization methods [22].

Although CFD is mainly used to simulate liquids and gases, the fluidlike behavior of plasma allows it to be described by the Navier-Stokes equations as well [22]. Therefore, CFD modeling has emerged as a powerful tool among plasma scientists.

CFD alone, however, cannot describe the chemical kinetics of the plasma system. At the same time as the development of CFD, simulations of chemical kinetics in combustion were also initiated. In 1963, publications emerged that attempted to improve the understanding of H_2 ignition through numerical simulations of reaction networks [23]. These simulations improved the understanding of ignition delays and the effects of radicals in combustion.

While these works on combustion kinetics describe only thermal chemistry, they have laid the groundwork for plasma kinetic simulations, in which electron-impact reactions, ion reactions, and reactions involving excited states are non-negligible [24].

1.4 The hydrogen rainbow

The emission spectrum of hydrogen shows four distinct lines: red, blue-green, blue-violet, and violet [25]. H_2 produced from the SMR, however, would be classified as “grey” [26,27]. This is not referring to any emission spectra, but rather to the sustainability of the H_2 production method, taking the reactants, energy sources, and CO_2 emissions into account. It is important to understand where we stand with plasma-based H_2 production compared to other H_2 production processes.

There are generally ten well-defined H_2 colors: green, orange, pink, red, yellow, grey, blue, turquoise, brown, and black [26]. Although more have arisen over the past few years, only these ten will be discussed here, as they are assigned a color for a specific production framework [28].

Figure 1-1 lists these ten different H_2 colors. For each color, the production process, energy source, H_2 source, and CO_2 emissions are given [26,27]. Here, SMR refers to Steam Methane Reforming, and CCUS refers to Carbon Capture, Utilization and Storage.

	 Energy Source	 H ₂ Source	 Production Process	 CO ₂ Emissions
Red	Nuclear	Water	Thermolysis	No direct
Pink	Nuclear	Water	Electrolysis	No direct
Orange	Mixed grid	Water	Electrolysis	Mix dependant
Yellow	Solar	Water	Thermolysis	No direct
Green	Renewables	Water	Electrolysis	No direct
Turquoise	Non-renewable	Natural gas	Pyrolysis	No direct
Blue	Non-renewable	Natural gas	SMR	Low (CCUS)
Brown	Non-renewable	Lignite	Gasification	High
Grey	Non-renewable	Natural gas	SMR	High
Black	Non-renewable	Hard coal	Gasification	High

Figure 1-1 – Ten widely-recognized H₂ colors defined using energy source, H₂ source, production process, and CO₂ emissions [26,27]. Here, SMR refers to Steam Methane Reforming, and CCUS refers to Carbon Capture, Utilization and Storage.

The best possible sustainable production of H₂ is green H₂, produced by electrolysis from renewable energy sources. Unfortunately, as stated in section 1.1 above (the introduction to H₂), this is still far from being commercially viable.

The brown, grey, and black H₂ are the ones currently in commercial use. Grey H₂ is the main H₂ production process worldwide [8]. Indeed, transitioning from grey to green is only possible by continuous improvement of the system. Our plasma H₂ production systems aim for an H₂ production method between turquoise and green. We can use renewable energy sources; however, we still want to use CH₄ or NH₃ as a reactant. In addition, with plasma-based H₂ production, we also move away from high or low CO₂ emissions (depending on CCUS systems) to no direct emissions, as is also the case for turquoise H₂.

1.5 Plasma pathways towards H₂

Instead of producing H₂ by electrolyzing H₂O, plasma aims to produce H₂ efficiently from CH₄ or NH₃. Specifically, warm plasma, due to its elevated gas temperature, is a good

candidate for H₂ production. These general processes can be split into three main production methods.

First, the direct treatment of CH₄ with plasma is considered “methane reforming”, leading to C₂ hydrocarbon formation and H₂ gas, together with possible carbon black deposits. Second, admixing CO₂ with CH₄ in plasma reforming is known as “dry reforming of methane” (DRM) and leads to the formation of H₂ and CO, a mixture called syngas. Finally, treatment of NH₃ with plasma yields N₂ and H₂ in a process called “ammonia cracking”. Each of these processes has its own uses, benefits, and challenges for industrial deployment. Therefore, each process also has its own performance metrics, which will be discussed in the subsequent chapters in which they are examined.

1.5.1 Methane reforming

Methane reforming aims to produce C₂ hydrocarbons from CH₄, in contrast to CH₄ pyrolysis (turquoise H₂), in which H₂ and solid carbon, C(s), are the main products. These reactions are energetically very different, as is apparent from their enthalpies of reaction [29,30].



Higher value C₂ hydrocarbons come at a cost. The higher the endothermic reaction enthalpy, the more energy is required. Furthermore, forming solid carbon products is kinetically easier than targeting C₂ hydrocarbons. Hence, H₂ production via plasma pyrolysis is already operational on an industrial scale [31–33].

H₂ production via methane reforming towards C₂ hydrocarbons is also industrially interesting, due to the large C₂H₄ market, essentially creating two valuable compounds, namely C₂H₄ and H₂, because the C(s) by-product is not always of high value. Here, the main challenge remains optimizing product selectivity at a reasonable EC, while limiting soot formation. As chemical kinetics is an important part of the system, modeling provides valuable insights into this process and thus into its optimization.

1.5.2 Dry reforming of methane

Methane reforming faces a major operational issue: the formation of unwanted soot in the plasma reactor. This soot will lower the production efficiency and possibly even extinguish the plasma itself. A shift towards lower soot formation is possible by adding CO₂ as a co-reactant to CH₄. This significantly reduces soot formation, either by oxidizing soot or by suppressing soot precursors. Furthermore, adding CO₂ shifts DRM further towards green hydrogen, since this process consumes CO₂.

Adding CO₂ as an additional reactant, however, creates a different product composition. Instead of forming H₂ and C₂ hydrocarbons, the main product is syngas.



Syngas is industrially very interesting. Small organic compounds such as methanol and formaldehyde are produced from syngas [34]. Furthermore, it is important for the formation of aviation fuels and lubricants via the Fischer-Tropsch process [35]. These processes rely on syngas with a specific ratio (H₂/CO). For instance, a syngas ratio of 2 is optimal for Fischer-Tropsch with a cobalt catalyst, while a ratio of 1 is also suitable with an iron catalyst [36,37]. Still, tuning the ratio on the production side is important, as these catalysts have significantly different activities and product selectivities [38].

Controlling the syngas ratio is therefore a major challenge in plasma-based DRM. An important side reaction influencing the ratio is the (reverse) water-gas shift ((R)WGS) [39]. The WGS increases the syngas ratio, while the RWGS lowers it. The following are the WGS and RWGS, respectively:



The challenge of optimizing the syngas ratio, while suppressing soot formation in DRM, requires a deep understanding of the underlying chemical processes and the impact of flow dynamics, making modeling an ideal research tool for plasma-based DRM.

1.5.3 NH₃ cracking

NH₃ cracking is somewhat different from the other H₂ production processes. Unfortunately, there are no large, easily accessible natural reservoirs of NH₃. Therefore, it must be produced first. The Haber-Bosch process is a well-established method for producing NH₃ on a large scale from N₂ and H₂ [40].

Thus, producing H_2 from NH_3 sounds counter-intuitive. However, this process serves a different purpose. The transport of H_2 is not an easy task due to high gas compression, low energy density, and high explosion risk [41,42]. Transporting H_2 in the form of NH_3 is a viable solution for getting energy from high-production to high-consumption zones [43]. While this solves the issues with H_2 transportation, NH_3 transportation does pose other risks. Indeed, NH_3 is highly corrosive and extremely toxic. On the other hand, NH_3 transport and other liquid energy vectors (like LNG) benefit from well-established industrial infrastructure [44]. While the Haber-Bosch process is already an efficient method for NH_3 production, the reverse process, NH_3 cracking, however remains inefficient [45].

Plasma-based NH_3 cracking could be a viable approach, as the overall reaction producing H_2 from NH_3 is slightly endothermic.



This endothermic reaction enthalpy suggests that NH_3 is more stable at room temperature than N_2 and H_2 , which is indeed the case. The large effort to create NH_3 from N_2 and H_2 in the Haber-Bosch process is to overcome the reaction's kinetic activation energy by increasing the gas temperature. However, this in turn shifts the thermodynamic equilibrium unfavorably, leading to the need for high pressures [40,46]. Indeed, for the NH_3 cracking process, the same activation energy must be overcome, but at elevated temperatures ($> 500 \text{ K}$), the thermodynamic equilibrium is favorable to cracking.

Therefore, plasma-based NH_3 cracking is also mainly a kinetically limited process, with a strong dependence on accurate chemical and plasma kinetics [47]. Here, both kinetic and CFD plasma modeling could greatly benefit the understanding of the optimal NH_3 cracking mechanism and ways to improve plasma-based NH_3 cracking processes.

1.6 Thermal chemistry vs electron-impact reactions in warm plasma

Section 1.2 above (the introduction to plasma) distinguishes among three types: non-thermal cold plasma, warm plasma, and thermal plasma. The H_2 -producing chemistry via any of the reactions discussed above can occur through either thermal or electron-impact chemistry. Which type of reaction dominates depends on the plasma type: non-thermal, cold plasmas are dominated by electron-impact reactions, whereas warm (and

thermal) plasmas are mainly governed by thermal chemistry, driving the dominant, interesting processes [48–51].

The claim that electron-impact chemistry dominates cold plasma processes is generally accepted. The claim that thermal reactions generally dominate warm plasma processes is less widely accepted; however, it can be inferred from the literature [52–63].

First, atmospheric pressure warm plasmas (e.g., DC or AC arcs, microwave plasmas, ...) have core gas temperatures of a few thousand Kelvin ($> 3500\text{ K}$), irrespective of the gas (CO_2 , N_2/O_2 , CH_4/CO_2 , CH_4 , NH_3) [52,53,56–63]. Second, the electrons in these warm plasmas are mainly located in the core. When pressure increases from sub-atmospheric to atmospheric pressure, the plasma contracts. This makes sense, as a hot gas at a few thousand Kelvin is a much better electrical conductor than its cold counterpart without the elevated electron temperature [54].

If the gas composition reaches chemical equilibrium before entering the electron-rich plasma core, we can conclude that the thermal system dominates warm-plasma reactions. It is important to understand that the chemical equilibrium based purely on thermodynamics already shifts away from CH_4 and NH_3 around 1000 K . Figure 1-2 shows the conversion in equilibrium for CH_4 or NH_3 to be converted at a constant temperature, starting from 100 % CH_4 , 100 % NH_3 , and a 50 % CO_2 / 50 % CH_4 mixture representing DRM. The thermodynamic data are taken from the CRECK kinetic modeling work for fuels [55].

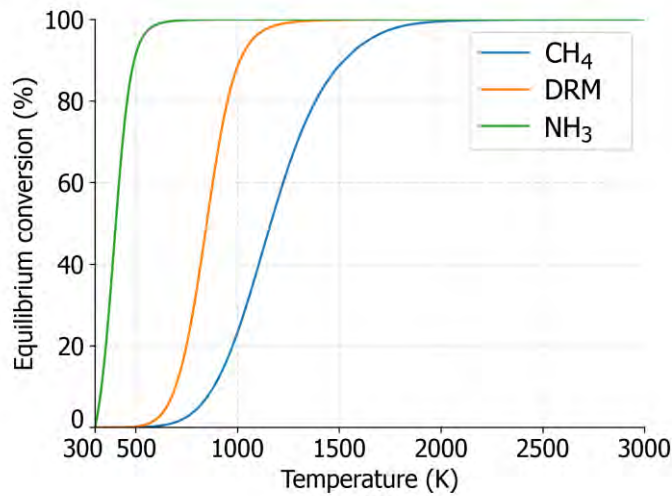


Figure 1-2 – Equilibrium conversion as a function of temperature for 100 % CH₄, 50 % CH₄ / 50 % CO₂ (DRM), and 100 % NH₃. Thermodynamic data are taken from the CRECK kinetic modeling work [55].

Hence, the conversion is fully dependent on the kinetic barriers to overcome. Because this thesis focuses on CH₄, CH₄/CO₂, and NH₃ plasmas, we will examine only the kinetic barriers for these systems. Figure 1-3 shows the time for 95 % of CH₄ or NH₃ to be converted at a constant temperature, starting from 100 % CH₄, 100 % NH₃, and a 50 % CO₂ / 50 % CH₄ mixture representing DRM. The kinetic data are taken from the CRECK kinetic modeling work for fuels [55].

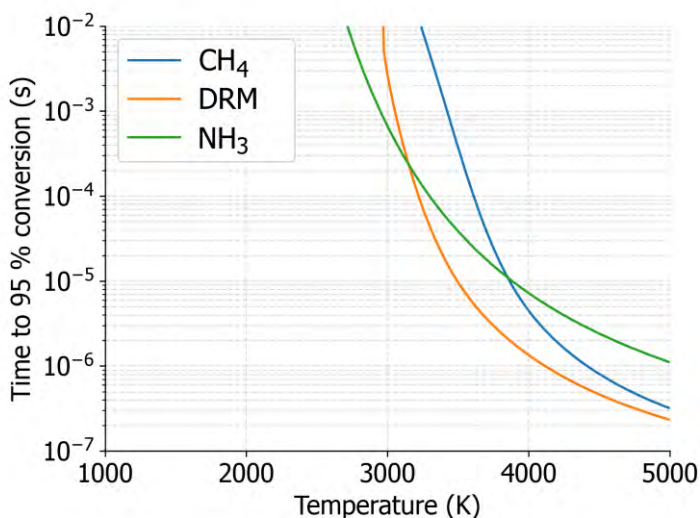


Figure 1-3 – Time to reach 95 % conversion thermally, for 100 % CH₄, 50 % CH₄ / 50 % CO₂ (DRM), and 100 % NH₃. Kinetic data taken from the CRECK kinetic modeling work for fuels [55].

For both DRM and CH₄ pyrolysis, 95 % of the input CH₄ is destroyed at 4000 K in a few microseconds. Furthermore, 95 % conversion reaches the sub- μ s range at 5000 K. This implies that if CH₄ were to reach the plasma core to be dissociated by electron-impact, it would need to be transported there within a microsecond.

The same conclusion applies to the NH₃ data. Even though NH₃ takes longer to reach 95 % conversion at 4000 K (10 μ s), it still reaches the one μ s range at 5000 K and therefore will also be thermally cracked, if the time to reach the plasma core is on the order of microseconds.

Whether these gas molecules can reach the plasma core is not only a function of the convective flow. We must take gas temperature, concentration gradients, and diffusion coefficients into account. This question can only be answered by building a multidimensional model that accounts for all these effects. If a multidimensional model is built, neglecting electron-impact reactions, we can safely state that electron-impact reactions will only crack CH₄ or NH₃ which is still present in the plasma core. As will be illustrated later in this thesis, the time for these molecules to reach the plasma core is on the order of hundreds of μ s, hence much longer than a few microseconds, and therefore, CH₄ and NH₃ cracking in warm plasmas basically occurs thermally.

Electron-impact reactions do have a large effect on chemistry when the gas or plasma is cold (or at least, < 3000 K). This is the case on long timescales for cold plasmas, not considered in this thesis, as used for instance in medical applications [64–67]. On the other hand, this is also the case for ns-pulsed plasmas, where the plasma is intentionally extinguished only a few ns or μ s after ignition, as the gas temperature is still cold when the electron temperature is already very high [68–70]. These pulses often carry energies in the mJ range and are delivered at rates of thousands per second [70–72]. The repeated ignition places emphasis on the chemistry occurring in the cold spark; thus, the full plasma chemistry must be considered, including electron-impact reactions, ion and excited state chemistry.

1.7 State-of-the-art on plasma modeling

The previous section distinguishes between warm plasmas and non-thermal pulsed plasmas. It emphasizes the need for a correct transport description for warm plasmas and the need for a complete plasma kinetics description for non-thermal pulsed plasmas. Therefore, describing the state-of-the-art on plasma modeling will be split into a warm plasma, multidimensional CFD modeling section and a global kinetic modeling section, as these methods are vastly different.

1.7.1 Multidimensional CFD modeling for warm plasmas

Intuitively, it makes the most sense to model CFD in three dimensions, since the world in which our reactors are built is also 3D. These higher dimensions, however, come at a large increase in computational cost. Therefore, a trade-off is often made to keep models in 3D, by not capturing the plasma chemistry. Instead, the focus is on gaining insight into the gas flow dynamics and heat transfer. For instance, Van Alphen et al. simulated a rotating gliding arc (RGA) in 3D, including flow and heat transfer, to obtain molecular residence times in the plasma arc [73]. Furthermore, Van Alphen et al. also used this approach to investigate quenching strategies for CO_2 microwave plasmas [74]. Including the chemistry in 3D is much more difficult. Sun et al. simulated a 3D gliding arc, including argon chemistry, to gain insights into breakdown phenomena [75]. Similarly, Trenchev et al. modeled a gliding arc with argon chemistry and found good agreement with calculated current densities [76]. While these models serve their own purposes, accurately calculating gas conversion in molecular gas plasmas and optimizing the plasma chemical process in 3D models is impossible because the full chemistry cannot be included.

Instead, researchers typically use 2D simulations when including plasma chemistry. The validity of this modeling approach often depends on how well the modeled system can be mapped to 2D. Sun et al., for instance, also developed a 2D gliding arc model and found that 2D models are a good representation of 3D results; as such, they recommend using 2D models to understand gliding arc characteristics [75].

Other significant works in 2D modeling include the 2D drift-diffusion model for plasma-assisted combustion by Takana et al. [54] and the quasi-neutral and non-quasi-neutral gliding arc models built by Kolev et al. [77], the 2D axisymmetric model to compare glow and arc discharges by Tsonev et al. [78], a 2D air model by Naidis et al. [79], quantifying the effect of gas flow and degree of nonequilibrium across a wide current range, and the air model of Babaeva et al., which describes plasma arc contraction as a function of gas flow and current [80]. While these models are for warm plasma gas conversion, progress in plasma modeling for cutting, welding, spraying, and nanomaterial synthesis can be found in the review by Zhang et al. [81]. Thermal plasma models focusing on turbulence at very high temperatures are being developed by Shigeta following the large-eddy simulation approach [82]. These thermal plasma fluid models are useful to understand welding plasmas, as is done extensively by Murphy et al. [83–85]. Modeling of thermal plasmas also provides insights into the effects of the arc on the electrodes, as is done by Benilov et al. [86]. Indeed, modeling of the cathode and electron emission mechanisms thereof is a fully separate domain of study. Extensive modeling of the plasma sheath via nonlocal thermodynamic equilibrium-sheath approaches has been done by Baeva et al. [87,88]. A fully self-consistent model of the electrode plasma interaction for an N_2 arc has been built by Wang et al. [89]. In this work, we ignore plasma-electrode interactions and the plasma sheath as it was shown to be of negligible importance for the bulk plasma by Tsonev et al. [78].

1.7.2 Global chemical kinetics modeling

Chemical kinetics modeling is typically applied to non-thermal (low-pressure) plasmas. Instead of solving flow dynamics and species transport, the computational effort is shifted to accurately describing the electron energies and all accompanying processes, including changes in densities for tens or hundreds of species. Correctly building a global kinetic plasma model differs from the kinetic combustion models introduced in the mid-20th century, because of the electron energy balance, which is well described by Hagelaar et al. [90]. The correct description of the interactions between high-energy

electrons and neutral species is made possible by the international LXCat project, which serves as a database for cross-sections of electron interactions with heavy species [91].

Notable past works in global modeling include the low-pressure air model by Gordiets et al. [92], the low-pressure nitrogen model by Guerra et al. [93], and the low-pressure oxygen model by Viegas et al. [94]. These models provide good experimental agreement, due to the diffuse nature of low-pressure plasmas.

Industry, however, is interested in atmospheric pressure plasmas. Here, the plasma is typically not spatially uniform, but contracted, so that global models cannot provide the most realistic description of experiments, but instead they can still serve to deepen our understanding of key plasma chemical mechanisms. Some important publications in atmospheric-pressure global models include the oxygen model of Albrechts et al. [95], which demonstrates fast recombination kinetics at atmospheric pressure, and the model of Slaets et al. for DRM [48], which shows the relative effects of plasma versus thermal conversion. They reach the same conclusion as the aforementioned combustion data: the effective plasma chemistry (induced by electrons) is negligible compared to the thermal chemistry in warm plasma.

Furthermore, an atmospheric-pressure global model was developed by Wang et al. to explore plasma chemical pathways for energy-efficient nitrogen fixation [96]. As global models do not describe real systems, their optimal use is indeed finding the optimal path towards any desired product. Researchers can explore non-equilibrium effects, such as elevated vibrational temperatures, or effects occurring on extremely short timescales, such as fast nanosecond chemistry, which informs plasma reactor designs. Two good examples are the works of Koelman et al. [97] and Tsonev et al. [98] for CO₂ dissociation.

1.8 Aim of this thesis

This thesis aims to develop both multidimensional CFD models for warm plasma reactors and global non-thermal plasma models to increase our understanding of plasma chemical processes and to inform future plasma reactor design. For each model, we will present a different chapter, each with its own research question.

This thesis consists of eight chapters. The general methodology follows this introduction in Chapter 1 and is presented in Chapter 2. Chapters 3 - 7 present five different models for different plasma reactors and chemistries, but all related to plasma-based H₂ production. Each of these chapters aims to provide a significant improvement in

(plasma-)chemistry through novel modeling approaches. Finally, a general conclusion is presented in Chapter 8.

In **Chapter 2**, the general methodology for both modeling types is described. As several plasma reactors are modeled in this thesis, Chapter 2 will describe only the equations, while specific details on the plasma reactors, such as geometry and boundary conditions, are explained in the respective chapters.

In **Chapter 3**, the model of the atmospheric-pressure glow discharge (APGD) reactor is presented. This is a multidimensional CFD model for DRM that includes oxygen to suppress soot formation. Previous experiments found a good syngas ratio from several mixtures of CO_2 , CH_4 , and O_2 . However, large differences in conversion at similar plasma powers suggest a significant shift in the chemistry. Hence, a CFD model that includes chemical kinetics is built for the first time to understand the shift in chemistry.

In **Chapter 4**, a global model is developed to understand NH_3 cracking pathways in non-thermal plasmas. This chapter uncovers the potential synergistic effects between thermal chemical reactions and plasma chemistry by combining both of them in a global model. Finally, a new strategy for “plasma-initialized” thermal cracking is described to enable energy-efficient NH_3 cracking.

Chapter 5 focuses on plasma-based NH_3 cracking in warm plasma. A multidimensional CFD model is developed to interpret experimental results. More specifically, the effect of turbulent transport is investigated, to determine whether warm plasma NH_3 cracking benefits from increased turbulence. The multidimensional model makes a clear distinction between NH_3 cracking inside the plasma and in the plasma afterglow region. The latter is more important than anticipated.

In **Chapter 6**, a global model is built to understand CH_4 non-thermal plasma reforming. The model aims to self-consistently calculate the gas temperature and pressure in a CH_4 nanosecond-pulsed plasma. This is a significant improvement over previous global models, in which the gas temperature and pressure were treated as user inputs. This model allows us to perform a detailed analysis of reaction pathways in CH_4 nanosecond pulses and to understand the effect of preheating the gas before pulsing.

Likewise, **Chapter 7** presents another multidimensional model, developed to assess soot formation in arc plasmas. We are able to describe the complex CH_4 chemistry and its conversion towards various products, in good agreement with experiments.

Furthermore, we observe that soot formation can be split into two mechanisms, one occurring in the plasma and one near the edge and in the afterglow.

Chapter 2

General Methodology

The previous chapter clearly distinguishes between multidimensional CFD models and global models. Hence, in this methodology chapter, we will keep this distinction. We will first discuss the common equations, i.e., the thermal chemical kinetics equations, and then describe the multidimensional CFD and global kinetic models separately. The exact plasma reactor geometry or setup for each model will be discussed in the relevant chapters; the only exception is the global model of Chapter 6, for which we need to explain the geometry here, as it is necessary to understand the equations.

2.1 Thermal chemical kinetics

All models presented in this thesis include thermal chemical kinetics to describe the chemistry (or a large part of it). The reaction rates are dependent on the rate coefficients and the concentrations of the reactants. For the general reaction:



with species A , B , C and D , having a_A , a_B , a_C and a_D as their stoichiometric coefficients, and $\Delta_r H^0$ representing the reaction enthalpy (in J), the reaction rate r_{rate} can be written as:

$$r_{rate} = k_r \times \prod_l n_l^l \quad [1]$$

Here, n_l^l is the concentration of species l on the left side of the reaction (in mol.m^{-3}) and k_r is the forward rate coefficient, with units to ensure the unit of r_{rate} is $\text{mol.m}^{-3}.\text{s}^{-1}$. This forward reaction rate coefficient can depend on gas temperature and/or pressure in multiple ways.

2.1.1 Rate coefficients

Following the Arrhenius equation, the rate coefficient depends only on the gas temperature, T_g [99]:

$$k_r = A \cdot T_g^b \cdot \exp\left(-\frac{E_a}{RT_g}\right) \quad [2]$$

Here, A is a pre-exponential factor (same unit as k_r) which is a function of T_g (K), b is a unitless empirical temperature exponent, E_a is the activation energy (J.mol^{-1}) and R is the universal gas constant ($8.314\text{ J.mol}^{-1}.\text{K}^{-1}$).

This description unfortunately fails in case of three-body reactions, where some species are not consumed, but are present as a third body (reacting neutral species). This reacting neutral is not included in equation 1, but should still be considered in the reaction rate. Directly adding it is not an option, as there is a saturation limit for reacting neutrals; indeed, increasing the third body concentration will not indefinitely increase the reaction rate. To circumvent this problem, Troe introduced fall-off curves that account for the pressure of the reacting neutral species [100].

The fall-off expression takes an Arrhenius equation at the lowest reacting neutral pressure, k_0 , an Arrhenius equation at infinite reacting neutral pressure, k_∞ , and a unitless blending function F_c :

$$k_r = \frac{k_0[M]k_\infty}{k_0[M] + k_\infty} F \quad [3]$$

$$\log F = \frac{\log F_c}{1 + \left[\frac{\log(k_0[M]/k_\infty)}{N} \right]^2} \quad [4]$$

$$N = 0.75 - 1.27 \log F_c \quad [5]$$

Here, $[M]$ is the reacting neutral concentration and the unit of $k_0[M]$ should match the unit of k_∞ , which matches the unit of k_r .

2.2 Detailed balancing

If each reaction is considered as an elementary reaction (one-step process) with a single activation energy barrier, the reverse reaction rate coefficient can be calculated from detailed balance. Consider the following reaction with forward reaction rate coefficient, $k_{r,F}$:



The reverse reaction rate coefficient, $k_{r,R}$, can be obtained from the equilibrium constant, K_{eq} , following:

$$\frac{k_{r,F}}{k_{r,R}} = K_{eq} = e^{\left(\frac{\Delta S(T_g)}{R} - \frac{\Delta H(T_g)}{RT} \right)} \cdot \left(\frac{1 \text{ bar}}{RT_g} \right)^{(c+d-a-b)} \quad [6]$$

With $\Delta S(T_g)$ the reaction entropy and $\Delta H(T_g)$ the reaction enthalpy, both as a function of the gas temperature at 1 bar.

ΔS and ΔH are calculated from the change in molar entropy, $S(T_g)$, and molar enthalpy, $H(T_g)$, respectively, of the various species in a reaction. The molar enthalpy and entropy are defined using the 9-term NASA polynomial [101], and if not available, other 9-term polynomials are taken from the work of Burcat [102]. The $H(T_g)$ and $S(T_g)$ polynomials are both obtained from the $C_p(T_g)$ polynomial, by integrating $C_p(T_g)$ and $C_p(T_g)/T_g$ with respect to T_g , respectively:

$$C_p(T_g) = R \left(a_1 T_g^{-2} + \frac{a_2}{T_g} + a_3 + a_4 T_g + a_5 T_g^2 + a_6 T_g^3 + a_7 T_g^4 \right) \quad [7]$$

$$H(T_g) = RT \left(-a_1 T_g^{-2} + a_2 \frac{\ln T_g}{T_g} + a_3 + a_4 \frac{T_g}{2} + a_5 \frac{T_g^2}{3} + a_6 \frac{T_g^3}{4} + a_7 \frac{T_g^4}{5} + \frac{b_1}{T_g} \right) \quad [8]$$

$$S(T_g) = R \left(-a_1 \frac{T_g^{-2}}{2} - \frac{a_2}{T_g} + a_3 \ln T_g + a_4 T_g + a_5 \frac{T_g^2}{2} + a_6 \frac{T_g^3}{3} + a_7 \frac{T_g^4}{4} + b_2 \right) \quad [9]$$

$\Delta S(T_g)$ and $\Delta H(T_g)$ are then, for the example reaction 2 above:

$$\Delta S(T) = cS_C(T) + dS_D(T) - aS_A(T) - bS_B(T) \quad [10]$$

$$\Delta H(T) = cH_C(T) + dH_D(T) - aH_A(T) - bH_B(T) \quad [11]$$

2.3 Chemistry reduction

We developed large thermal chemistry sets (>200 species), which can be easily solved with a global model. However, computational costs increase dramatically when they are applied to a multidimensional simulation that accounts for many other physical processes as well (see next section). Therefore, we conducted a sensitivity analysis on the full chemistry sets of both DRM and NH₃ cracking, to reduce them by removing species and reactions that are “negligible” (see below for the criterion) for the conditions under study, similar to the analysis by Stagni et al. [103].

This sensitivity analysis evaluates how the model inputs, i.e., the species and reactions included in the model, affect the output, and thus how we can reduce our chemistry set (both species and reactions) within a maximum allowed deviation.

We carried out several global simulations for different temperature profiles (e.g., within the expected temperature range for DRM with oxygen in the APGD, 300–4000 K). Note that the actual temperature range relevant for the APGD is 2000–3500 K, but we used a broader range to be sure that we do not use the CFD model outside boundaries, after our chemistry reduction. We defined a ‘deviation’ quantity as the maximum deviation of the reduced set from the total chemistry set at any point in the simulation. Note that both the DRM with oxygen system and the NH₃ system operate at atmospheric pressure; therefore, a pressure sweep to assess sensitivity is unnecessary.

Specifically, we define a maximum deviation factor of 0.01, which means that when the calculated molar fraction, $x_{reduced}$, of any species of a reduced set at any point during

the simulation is greater or smaller than $x_{full} \pm 0.01$, the reduced set is considered invalid. This in turn allows for the removal of species with $x \leq 0.01$, as long as they are not an important intermediate species for any other species with $x \geq 0.01$.

Figure 2-1 illustrates the sensitivity-reduction algorithm used to reduce our thermal chemistry sets for multidimensional modeling. The same principle was applied to the reaction sensitivity analysis. First, every species was attempted to be removed, and a deviation was calculated for each species accordingly. Second, the species were ranked in order of increasing deviation. Simulations were carried out with multiple species deleted. Specifically, for the 41 species considered in the case of DRM with oxygen addition, 41 simulations were conducted. The first simulation removed the species with the smallest deviation (T in Figure 2-1); the second removed two species with the two smallest deviations (R and T in Figure 2-1); the third removed three species, etc. We then calculated the deviations for the corresponding groups of species and removed species from the group with the largest acceptable deviation (R and T, with deviation t ; see Figure 2-1). We applied this procedure to every condition under study (as indicated by the temperature profile in Figure 2-1) and finally removed from the model those species that exhibited the largest acceptable deviation for each condition.

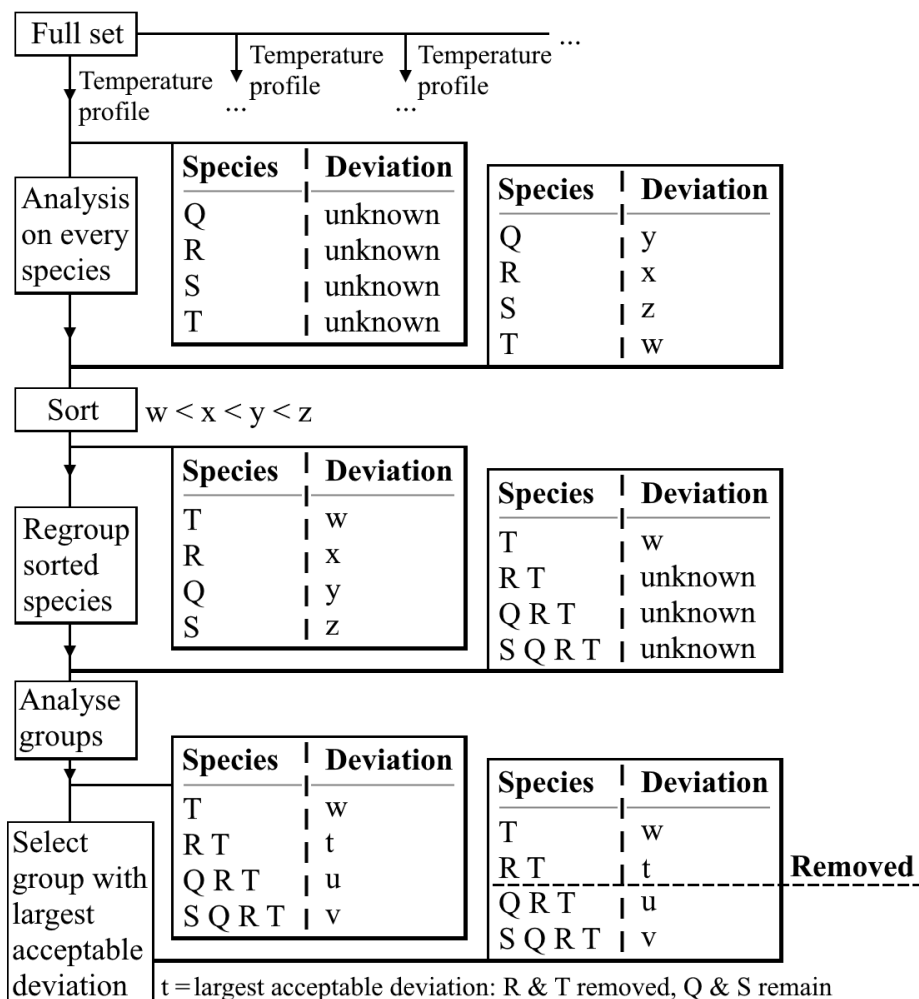


Figure 2-1 - Sensitivity reduction algorithm used to reduce the thermal chemistry sets for multidimensional modeling. For each species, we calculate the deviation between the reduced and full sets. We then sort them by deviation from smallest to largest and we group them, for which we again calculate the deviation.

Finally, we select the group with the largest acceptable deviation (in this case: t), and we remove all species belonging to that group. We apply this procedure for each condition (as indicated here by "Temperature profile"). We finally remove the (group of) species that exhibit the largest acceptable deviation for all conditions.

After removing the least important species, we applied the same steps to the possible removal of the remaining reactions (i.e., those that remained after removing the negligible species). We again ran a simulation for each omitted reaction. The deviation was calculated for each simulation, ranking them from smallest to largest as we get to the last step. Again, we performed simulations equal in number to the number of

reactions in the chemistry sets: in the first simulation, we removed the reaction with the smallest deviation; in the second, we removed the two reactions with the two smallest deviations, etc. The results of the reductions are presented in the multidimensional modeling chapters.

2.4 Multidimensional CFD models

Ideally, plasma reactors should be described using a 3D coupled model, solving gas flow, heat transfer, species transport and chemistry, the Poisson and current conservation equations. However, the computational cost of mesh-converged calculations makes such models unfeasible [104]. In this thesis, we therefore propose a 2D axisymmetric model to describe 3D plasma reactors, which are indeed mainly axisymmetric (with the exception of the gas inlet system; see further). This limits the number of mesh cells needed to effectively reduce the computational costs. Furthermore, we reduce a complex thermal chemistry set using the above sensitivity analysis, to enable a coupled implementation in the 2D axisymmetric model, providing a more accurate description of the interactions among the chemistry, gas flow, and heat equations than previously considered model approaches [73,74,105–107]. In the first CFD model that we developed (Chapter 3), the Poisson and current conservation equations are not solved because, as mentioned above, thermal chemistry is dominant in warm plasmas, and we can use a heat source to describe gas heating from the plasma, either user-defined or from Joule heating. This is indeed a valid approach, considering a (known) electron density profile and assuming the electron temperature to be equal to the gas temperature [74]. However, in our later CFD models (Chapters 5 and 7) we further improved the physics described, and we do solve the current conservation equations (see details in section 2.4.4 below).

Building multidimensional CFD models for systems with large chemistry sets requires a carefully constructed modeling framework. Figure 2-2 presents a flowchart for building multidimensional CFD plasma models, starting from the chemistry set and the reactor geometry. Each step, along with its set of equations, will be described in detail below.

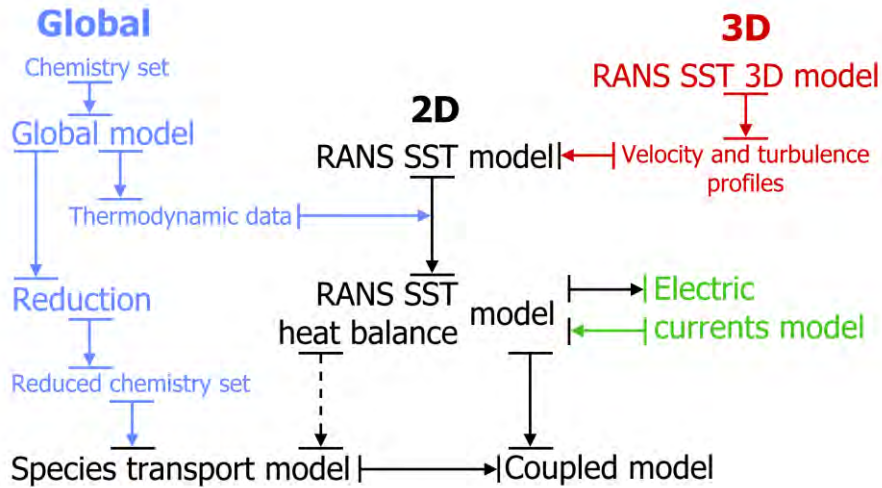


Figure 2-2 - Flowchart of the coupled 2D axisymmetric model, with input from 0D and 3D models. The components of the 0D model (reduction of the chemistry set and calculation of the thermodynamic variables) are in blue, the 3D component (input velocity profile) in red, and the 2D models are shown in black. The models of Chapters 5 and 7 also solve the current conservation equation (in green) as a heat source. Input and output data are shown in a smaller font, while models are depicted in a larger font. Full arrows indicate that the previous equations are also included in the next step, while the dashed arrow indicates only using the previous result as a background.

We start with a 3D fluid model based on the experimental reactor geometry. This is a Reynolds-averaged Navier-Stokes (RANS) model using Menter’s Shear Stress Transport (SST) description for the turbulence. The 3D RANS SST model uses only the experimental gas flow rate as input condition. We use the gas velocity profile obtained from this 3D model as the input boundary condition for the 2D axisymmetric model; the spatial implementation depends on the reactor geometry and will be discussed in detail in the relevant chapters. We use the full chemistry set to calculate the thermodynamic properties, described in section 2.2 above and section 2.4.7 below. Using the flow solution, we include the plasma power (implemented either as a heat source or by solving the current conservation equations (in green), as explained above, see section 2.4.4 below) to solve the heat balance and 2D RANS SST equations (sections 2.4.5 and 2.4.3 below). After the reduction of the thermal chemistry set in the 0D model (section 2.3 above), we implement the reduced chemistry set in the 2D model, and we solve the transport of species (including chemistry) equations (section 2.4.7 below) on top of the results from the heat balance and RANS SST model in the previous step. Note that in this intermediate step, the heat balance and RANS SST equations are not solved again; instead, we use the previous result as input. Finally, we use the resulting species

transport solution and the previous heat balance and RANS SST solution as initial conditions for the coupled model. From now on, the thermodynamic properties influencing the heat balance and RANS SST equations depend on the mass fractions calculated by the transport of species equation (including chemistry), with the formulations given by the equations in section 2.4.6 below.

2.4.1 3D flow models

The 3D fluid dynamics model is solved using COMSOL Multiphysics® [108]. We describe the gas flow in the reactor using an SST turbulent fluid flow model with weakly compressible flow. Specifically, in 3D, we solve these RANS equations [109,110]:

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad [12]$$

$$\rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[-p\mathbf{I} + (\mu + \mu_T)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}(\mu + \mu_T)(\nabla \cdot \mathbf{u})\mathbf{I} - \frac{2}{3}\rho k\mathbf{I} \right] \quad [13]$$

In these equations, ρ is the gas density calculated by the thermodynamic model (see section 2.4.6 below), $\mathbf{u}$ is the gas flow velocity vector, p is the gas pressure, $\mathbf{I}$ is the unity tensor, μ is the dynamic viscosity, μ_T is the turbulent dynamic viscosity, k is the turbulent kinetic energy, and superscript T describes transposition. ρ and μ in these equations are based on the gas thermodynamic properties at 300 K, since the gas temperature is held at 300 K in the 3D model.

The full description of the fluid flow equations can be found in section 2.4.3, which details the 2D fluid flow equations.

2.4.2 Translation to 2D axisymmetric models

The transfer of the 3D input flow field to a 2D axisymmetric model is not just geometry dependent. An adequate inflow plane must be chosen, as detailed in the relevant chapters below. The flow field must also be transformed from Cartesian to cylindrical velocity components. We translate the Cartesian velocity components (of the 3D model) into cylindrical components using the following equations, obtained from the derivation of the transformation of Cartesian coordinates into cylindrical coordinates with respect to time [111].

$$v_r = \frac{dr}{dt} = \frac{d}{dt} \left(\sqrt{x^2 + y^2} \right) = \frac{xv_x + yv_y}{\sqrt{x^2 + y^2}} \quad [14]$$

$$v_\varphi = r \frac{d\varphi}{dt} = \sqrt{x^2 + y^2} \frac{d}{dt} \left(\tan^{-1} \left(\frac{y}{x} \right) \right) = \frac{xv_y - yv_x}{\sqrt{x^2 + y^2}} \quad [15]$$

$$v_z = v_z \quad [16]$$

The same equations are obtained when translating Cartesian velocity vectors into cylindrical velocity vectors via trigonometric manipulation.

2.4.3 Fluid flow equations

Like the 3D fluid flow model, the 2D axisymmetric model is solved using COMSOL Multiphysics® [108]. Both models solve the general RANS SST momentum conservation equations. The two governing equations are repeated here [110]:

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad [17]$$

$$\rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[-p\mathbf{I} + (\mu + \mu_T)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}(\mu + \mu_T)(\nabla \cdot \mathbf{u})\mathbf{I} - \frac{2}{3}\rho\varepsilon\mathbf{I} \right] \quad [18]$$

Here, ρ is the gas density, $\mathbf{u}$ is the gas flow velocity vector, p is the gas pressure, $\mathbf{I}$ is the unity tensor, μ is the dynamic viscosity, μ_T is the turbulent dynamic viscosity, ε is the turbulent kinetic energy, and superscript T describes transposition. ρ and μ in the final coupled model depend on the local gas composition, as detailed in section 2.4.6.

Equation 18 includes the sum of the dynamic viscosity (μ) and turbulent dynamic viscosity (μ_T). While the former is obtained from section 2.4.6, the latter is calculated as follows:

$$\mu_T = \rho \frac{a_1 \varepsilon}{\max(a_1 \omega, S f_{v2})}, S = \sqrt{2\mathbf{S}:\mathbf{S}}, \mathbf{S} = \frac{1}{2}(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \quad [19]$$

Here, a_1 is a turbulence modeling parameter, and the value is shown in Table 2-1 at the end of this section, and $\mathbf{S}:\mathbf{S}$ is the tensor contraction of $\mathbf{S}$.

Additionally, the governing equations for the turbulent kinetic energy, ε , found in equation 18, and the turbulent dissipation rate, ω , are given by [110]:

$$\rho(\mathbf{u} \cdot \nabla) \varepsilon = \nabla \cdot [(\mu + \mu_T \sigma_\varepsilon) \nabla \varepsilon] + P - \beta_0^* \rho \omega \varepsilon \quad [20]$$

$$\rho(\mathbf{u} \cdot \nabla) \omega = \nabla \cdot [(\mu + \mu_T \sigma_\omega) \nabla \omega] + \frac{\gamma}{\mu_T} \rho P - \rho \beta \omega^2 + 2(1 - f_{v1}) \frac{\sigma_{\omega 2} \rho}{\omega} \nabla \varepsilon \cdot \nabla \omega \quad [21]$$

Here P is the turbulent kinetic energy source term, β_0^* and $\sigma_{\omega 2}$ are turbulence modeling parameters, $\gamma, \beta, \sigma_\varepsilon$ and σ_ω are turbulence parameters depending on the blending functions f_{v1} and f_{v2} .

The turbulent kinetic source term used in equations 20 and 21 is calculated as follows:

$$P = \min(P_\varepsilon, 10\beta_0^* \rho \omega \varepsilon) \quad [22]$$

$$P_\varepsilon = \mu_T \left[\nabla \mathbf{u} : (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} (\nabla \cdot \mathbf{u})^2 \right] - \frac{2}{3} \rho \varepsilon \nabla \cdot \mathbf{u} \quad [23]$$

Here β_0 is a modeling parameter, and its value is also shown in Table 2-1 at the end of this section.

Interpolation of values for parameters depending on a blending function is performed as follows:

$$\varphi = f_{v1} \varphi_1 + (1 - f_{v1}) \varphi_2 \quad \text{for any} \quad \varphi = \gamma, \beta, \sigma_k \text{ or } \sigma_\omega \quad [24]$$

The blending functions used in equations 21 and 24 are calculated as follows:

$$f_{v1} = \tanh(\theta_1^4) \quad [25]$$

$$\theta_1 = \min \left[\max \left[\frac{\sqrt{\varepsilon}}{\beta_0^* \omega l_w}, \frac{500\mu}{\rho \omega l_w} \right], \frac{4\rho \sigma_{\omega 2} \varepsilon}{CD_{\varepsilon \omega} l_w^2} \right] \quad [26]$$

$$CD_{\varepsilon \omega} = \max \left(\frac{2\rho \sigma_{\omega 2}}{\omega} \nabla \omega \cdot \nabla \varepsilon, 10^{-10} \right) \quad [27]$$

$$f_{v2} = \tanh(\theta_2^2) \quad [28]$$

$$\theta_2 = \max \left(\frac{2\sqrt{\varepsilon}}{\beta_0^* \omega l_w}, \frac{500\mu}{\rho \omega l_w} \right) \quad [29]$$

Here, l_w is the distance of the current position to the closest wall. Below is a table of all modeling parameters used.

Table 2-1 - Turbulence model parameters, used in the RANS SST equations [112]

Parameter	Value	Parameter	Value
α_1	0.31	β_0^*	0.09
β_1	0.075	β_2	0.0828
γ_1	0.556	γ_2	0.44
σ_{k1}	0.85	σ_{k2}	1.0
$\sigma_{\omega 1}$	0.5	$\sigma_{\omega 2}$	0.856

2.4.4 Current conservation equations

The models of Chapters 5 and 7 also solve the current conservation equations for a more physically accurate heat source. The electrical current density is partially determined by the total current given as input and is governed by the current conservation equations, which are the Ohmic current continuity equations in a hot gas [113]:

$$\mathbf{E} = -\nabla V \quad [30]$$

$$\nabla \cdot \mathbf{J} = 0 \quad [31]$$

$$\mathbf{J} = \sigma \mathbf{E} \quad [32]$$

Here, $\mathbf{E}$ is the electric vector field, V is the electric potential, $\mathbf{J}$ is the current density and σ is the electrical conductivity. In this case, σ is gas temperature-dependent and provided in a lookup table. This lookup table is calculated using Lieberman's cold DC plasma conductivity [114]:

$$\sigma = \frac{e^2 n_e}{m_e \nu_m} \quad [33]$$

Here, ν_m is the electron collision frequency, e the elementary charge, m_e the electron mass, and n_e the electron density, calculated from Gibbs free energy minimization using NASA polynomials [101]. The electron collision frequency is the sum over the individual collision frequencies of all neutral species. The electron collision frequency is calculated for each neutral species as an integral over the electron cross-sections of the LXCat database [115–119].

$$\nu_m = \sqrt{2/m_e} \sum_j N_j \int_0^\infty f(E_e) \sigma_{j,e}(E_e) E_e dE_e \quad [34]$$

Here, N_j is the density of neutral species j at equilibrium, f is the electron energy distribution function, which is assumed to be Maxwellian with the electron temperature equal to the gas temperature. $\sigma_{j,e}$ is the electron-neutral momentum transfer cross-section and E_e is the electron energy.

2.4.5 Heat transfer equations

The temperature is governed by the heat transfer equation [120]:

$$\rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot (-(k + k_T) \nabla T) + \sum_i \bar{H}_i r_i + \sum_i \mathbf{j}_i \cdot \nabla \bar{H}_i = \mathbf{E} \cdot \mathbf{J} \quad [35]$$

Here, ρ is the gas density, C_p is the heat capacity at constant pressure, both calculated based on the local gas composition, $\mathbf{u}$ is the velocity field vector, T is gas temperature, k is the thermal conductivity based on local gas composition, k_T is the turbulent thermal conductivity, $\bar{H}_i$ is the specific enthalpy of species i , r_i is the reaction rate of species i in mass units and $\mathbf{j}_i$ is the diffusive flux vector field of species i , also in mass units.

2.4.6 Gas property equations

As C_p and k depend on the gas composition, they are calculated as follows [120,121]:

$$C_p = \sum_i w_i \times \frac{C_{p,i}}{M_i} \quad [36]$$

Where w_i is the weight fraction of species i , M_i is the molar mass of species i and $C_{p,i}$ refers to the heat capacity taken from the NASA polynomial of species i .

The thermal conductivity of the mixture is described by:

$$k = 0.5 \left(\sum_i x_i k_i + \frac{1}{\sum_i x_i / k_i} \right) \quad [37]$$

where x_i is the molar fraction of species i , and k_i is the thermal conductivity of species i , calculated using:

$$k_i = 2.669 \times 10^{-6} \frac{\sqrt{T M_i \times 10^3}}{\sigma_i^2 \Omega_k} \times \frac{1.15 C_{p,i} + 0.88 R_g}{M_i} \quad [38]$$

Here, σ_i is the characteristic length of the Lennard-Jones potential, and Ω_k is the dimensionless collision integral given by:

$$\Omega_k = \frac{b_1}{(T^*)^{b_2}} + \frac{b_3}{\exp(b_4 T^*)} + \frac{b_5}{\exp(b_6 T^*)} + \frac{4.998 \cdot 10^{-40} \mu_{D,i}^4}{k_b^2 T^* \sigma_i^6}, \quad T^* = T \frac{k_b}{\varepsilon_i} \quad [39]$$

In this equation, b_x are empirical constants, T^* is the nondimensional temperature, $\mu_{D,i}$ is the dipole constant of species i , ε_i is the potential energy minimum value and k_b is Boltzmann's constant. These values are tabulated data taken from the literature [122].

Lastly, μ and ρ also depend on the chemical composition, where the former is calculated using:

$$\mu = \sum_{i=1}^n \frac{\mu_i}{1 + \frac{1}{x_i} \sum_{j=1, j \neq i}^n x_j \phi_{ij}}, \quad \phi_{ij} = \frac{(1 + (\mu_i/\mu_j)^{0.5} (M_j/M_i)^{0.25})^2}{(4/\sqrt{2})(1 + M_i/M_j)^{0.5}} \quad [40]$$

In this formula, x_i is the molar fraction. The dynamic viscosity of species i , μ_i , is calculated similarly to k_i in equation 38, using:

$$\mu_i = 2.669 \times 10^{-6} \frac{\sqrt{T M_i \times 10^3}}{\sigma_i^2 \Omega_D} \quad [41]$$

Here, Ω_D is expressed similarly to equation 39:

$$\Omega_D = \frac{b_1}{(T^*)^{b_2}} + \frac{b_3}{\exp(b_4 T^*)} + \frac{b_5}{\exp(b_6 T^*)} + \frac{4.998 \times 10^{-40} \mu_{D,i}^4}{k_b^2 T^* \sigma_i^6}, \quad T^* = T \frac{k_b}{\varepsilon_i} \quad [42]$$

ρ is calculated using the ideal gas law:

$$\rho = \frac{p M_N}{R_g T} \quad [43]$$

Here, p is the pressure, R_g is the gas constant, T is the temperature and M_N is the mean molar mass of the mixture.

The binary diffusion coefficient of species i in species j is calculated using:

$$D_{i,j} = 2.665 \times 10^{-22} \sqrt{\frac{T^3 (M_i + M_j)}{(2 \times 10^3 M_i M_j)}} \frac{1}{p \sigma_i \sigma_j \Omega_{D2}} \quad [44]$$

Here, Ω_{D2} is expressed similarly to equation 39:

$$\Omega_{D2} = \frac{c_1}{(T_2^*)^{c_2}} + \frac{c_3}{\exp(c_4 T_2^*)} + \frac{c_5}{\exp(c_6 T_2^*)} + \frac{c_7}{\exp(c_8 T_2^*)} + \frac{4.748 \times 10^{-40} \mu_{D,i}^2 \mu_{D,0}^2}{k_b^2 T \sigma_i^3 \sigma_j^3} \quad [45]$$

$$T_2^* = T \frac{k_b}{\sqrt{\varepsilon_i \varepsilon_j}} \quad [46]$$

From the turbulence variables, the turbulent thermal conductivity (k_T) is calculated as follows:

$$k_T = \frac{\mu_T C_p}{Pr_T} \quad [47]$$

Here Pr_T is the turbulent Prandtl number, which is calculated following the Kays-Crawford formulation:

$$Pr_T = \left(\frac{1}{2Pr_{T\infty}} + \frac{0.3}{\sqrt{Pr_{T\infty}}} \frac{\mu_T C_p}{k} - \left(0.3 \frac{\mu_T C_p}{k} \right)^2 \left(1 - e^{-k/0.3 \mu_T C_p \sqrt{Pr_{T\infty}}} \right) \right)^{-1} \quad [48]$$

Here $Pr_{T\infty}$ is the Prandtl number at infinity, set to 0.85.

2.4.7 Transport of species equations

The weight fractions of species are governed by the transport of species equation [121]:

$$\nabla \cdot \mathbf{j}_i + \rho(\mathbf{u} \cdot \nabla)w_i = r_i \quad [49]$$

Here w_i represents the weight fraction of species i . The reaction rate of a species, r_i , includes all production and loss terms for species i . Details on reaction rates and rate coefficients are in section 2.1.1. The diffusive flux vector is calculated from the Maxwell-Stefan diffusion model as follows [121]:

$$\mathbf{j}_i = - \left(\rho D_i^m \nabla w_i + \rho w_i D_i^m \frac{\nabla M_n}{M_n} + \rho w_i F D_{T,i} \nabla w_i - \mathbf{j}_{c,i} \right) \quad [50]$$

Here D_i^m is the diffusion coefficient for species i , M_n is the mean molar mass, $D_{T,i}$ is the turbulent diffusivity coefficient of species i and $\mathbf{j}_{c,i}$ is the multi-component diffusive flux correction term.

D_i^m , M_n and $\mathbf{j}_{c,i}$ are calculated via:

$$D_i^m = \frac{1 - w_i}{\sum_{k \neq i} \frac{x_k}{D_{i,k}}}, M_n = \left(\sum_i \frac{w_i}{M_i} \right)^{-1}, \mathbf{j}_{c,i} = \rho w_i \sum_k \frac{M_i}{M_n} D_k^m \nabla x_k \quad [51]$$

The turbulent diffusion coefficient for species i , used in equation 50, ($D_{T,i}$) is calculated as follows:

$$D_{T,i} = \frac{\nu_T}{Sc_{T,i}} \quad [52]$$

Here, ν_T is the turbulent kinematic viscosity and Sc_T is the turbulent Schmidt number. The turbulent kinematic viscosity is calculated as follows:

$$\nu_T = \frac{\mu_T}{\rho} \quad [53]$$

The turbulent Schmidt number is calculated following the Kays-Crawford formulation:

$$Sc_{T,i} = \left(\frac{1}{2Sc_{T\infty}} + \frac{0.3Pe_{T,i}}{\sqrt{Sc_{T\infty}}} - (0.3Pe_{T,i})^2 \left(1 - e^{-1/0.3Pe_{T,i}\sqrt{Sc_{T\infty}}} \right) \right)^{-1} \quad [54]$$

Here Pe_T is the turbulent Peclet number calculated as follows:

$$Pe_{T,i} = \frac{\mu_T}{\rho D_i^m} \quad [55]$$

2.5 Global models

The main characteristic of global models is the homogeneous approximation of the plasma. While this is generally valid for low-pressure plasmas, as discussed in Chapter 1, it becomes questionable in atmospheric-pressure systems with high spatial temperature gradients. In our opinion, global models can be used effectively in atmospheric plasmas using one of two methods: either as a parameter exploration tool, or in non-thermal plasmas, where applied gas flow fields are reasonably insignificant.

In Chapter 4, the global model is used to explore plasma parameters. The electron and gas temperatures are varied to determine the optimal time frame and EC for plasma-based NH_3 cracking. To find the optimal EC, specific heat balance equations are solved in detail in section 2.5.2 below. In Chapter 6, a two-zone global model is presented to reproduce and understand nanosecond-pulsed plasmas for CH_4 reforming. This model approximates reality by defining a discrete boundary between the plasma and the surrounding gas. Since this requires a spatial image to understand the equations, the geometry and equations specific to this model are detailed in section 2.5.3 below. Equations general to both global models are explained in section 2.5.1.

2.5.1 General global modeling equations

The main difference between global thermal models and global plasma models is the incorporation of electron-impact collisions with heavy species. As we explained thermal chemical kinetics already in section 2.1 above, we focus here on the electron kinetics. The rates of all electron-impact reactions are obtained from electron collisional cross sections, which depend on the electron energy (ε), and they are calculated from the electron energy distribution function (EEDF) ($f(\varepsilon)$). The latter is calculated following the time-dependent two-term Boltzmann equation approximation. The electron-impact reaction rate coefficient (k_e in $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) is calculated according to [123]:

$$k_e = \gamma \int_0^\infty \varepsilon \sigma_k(\varepsilon) f(\varepsilon) d\varepsilon \quad [56]$$

Here, $\gamma = \sqrt{\frac{2q}{m_e}}$, with m_e representing the electron mass (kg) and q the electron charge (C), σ_k is a cross section of electron-impact collision with heavy species (m^2). The sources of all cross sections can be found in the respective chapters.

The rates of these processes highly depend on electron energy. Therefore, the electron energy balance must also be solved. The electron energy is calculated using the two-term approximation to the Boltzmann equation, which includes electron-electron collisions [90]. The electrons gain energy from the electric field, following the local field approximation. The reduced electric field (i.e., ratio of electric field to gas number density, E/N , in Td) is calculated from:

$$E/N = \frac{1}{N} \sqrt{\frac{P_d}{\sigma}} = \frac{1}{N} \sqrt{\frac{P_d}{q\mu n_e}} \quad [57]$$

Here, N is the neutral number density (m^{-3}), P_d is the input power density ($\text{W} \cdot \text{m}^{-3}$) and σ is the electrical conductivity ($\text{S} \cdot \text{m}^{-1}$). Electrical conductivity can be rewritten as the product of q (electron charge, C), μ (electron mobility, $\text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) and n_e (electron density, m^{-3}). The electron mobility is calculated by integrating over the EEDF ($\text{eV}^{-3/2}$) following:

$$\mu N = -\frac{\gamma}{3} \int \frac{\varepsilon}{\sigma_m} \frac{\partial f(\varepsilon)}{\partial \varepsilon} d\varepsilon \quad [58]$$

Here, ε is the electron energy calculated using the local field approximation (eV), σ_m is the total collisional cross section (m^2) and $f(\varepsilon)$ is the EEDF.

We do not solve the electron number density balance, but instead, the electron density (n_e) is obtained from quasi-neutrality, following:

$$n_e = n_+ - n_- \quad [59]$$

Here, n_+ is the total positive ion density (m^{-3}) and n_- is the total negative ion density (m^{-3}).

Evidently, the global plasma model also solves the mass balance equations for all plasma species (except the electrons) as a function of time. The change in mass of species i over time follows:

$$\frac{d\rho w_i}{dt} = R_i \cdot M_i + \dot{S}_i \quad [60]$$

Here, w_i is the weight fraction of species i (unitless), R_i is the total production or destruction rate for species i ($\text{mol.m}^{-3}.\text{s}^{-1}$), M_i is the molar mass of species i (kg.mol^{-1}) and $\dot{S}_i$ is the total transport source term of species i ($\text{kg.m}^{-3}.\text{s}^{-1}$). Both the density and the weight fraction must be considered in the time derivative due to the changing mass within the plasma volume. The mass density (ρ) is calculated following the ideal gas law.

$$\rho = \frac{pM_n}{RT_g} \quad [61]$$

Here, p is the pressure (Pa) obtained from the conservation of mass or set as constant, M_n is the mean molar mass (kg.mol^{-1}), R is the universal gas constant ($\text{J.mol}^{-1}.\text{K}^{-1}$) and T_g is the gas temperature (K).

2.5.2 Heat balance equations to calculate EC

To understand the performance of warm plasma in terms of EC, tracking the energy introduced, and more specifically, the gas temperature, is essential. This can be done in two ways: either the gas temperature can be calculated by applying a plasma variation to the heat balance equation, or the gas temperature can be kept constant, and the energy required to maintain this temperature can be added or removed.

When we solve the gas temperature for a mixture consisting of j reactions, the following heavy particle energy balance is solved:

$$V_r C_p \rho \frac{dT_g}{dt} = -V_r \sum_j H_j r_j + V_r \sum_{j,elastic} S_{el,j} + V_r \sum_{j,e-diss} h_{add,j} r_j \quad [62]$$

Here, V_r is the reactor volume (m^3), C_p is the heat capacity of the gas at constant pressure ($J.kg^{-1}.K^{-1}$), ρ is the gas density ($kg.m^{-3}$), T_g is the gas temperature (K), H_j is the enthalpy of reaction j ($J.mol^{-1}$), r_j is the reaction rate of reaction j ($mol.m^{-3}.s^{-1}$), $S_{el,j}$ is the energy to heavy species from elastic collisions of reaction j as described by Hagelaar et al. [90] ($W.m^{-3}$), $j, e - diss$ is referring to all reactions involving electron-impact dissociation and $h_{add,j}$ is the additional energy difference between the predissociation state and the dissociation products of reaction j ($J.mol^{-1}$).

In some simulations, we set the gas temperature to a constant value. Then, the additional energy can just be equal to the inverse of the endothermic or exothermic energy of the reactions shown in equation 62, hence it can be evaluated as:

$$E_{@const.Tg} = \int_{t_0}^{t_{res}} V_r \sum_j H_j r_j - V_r \sum_{j,elastic} S_{el,j} - V_r \sum_{j,e-diss} h_{add,j} r_j dt \quad [63]$$

When simulations start at an elevated temperature (above 300 K) we also need to consider the energy needed for this heating. This energy depends on the gas mixture and is less prone to errors when calculated using the specific enthalpy:

$$E_{@init.Tg} = \rho_{initial} V_{r,initial} (H_{specific,Tg} - H_{specific,300K}) \quad [64]$$

Where $\rho_{initial}$ is the gas density of the starting mixture ($kg.m^{-3}$), $V_{r,initial}$ is the initial reactor volume (m^3), and $H_{specific,T}$ is the specific enthalpy at temperature T ($J.kg^{-1}$).

This calculation is used in Chapter 4 below, to calculate the EC for plasma-based NH_3 cracking with our global model.

2.5.3 Two-zone model description

Our two-zone model, used in Chapter 6 below, consists of a global plasma model (plasma model) and a global thermal kinetics model (cold model). The global plasma model is built within the COMSOL plasma module, while the global thermal kinetics model is built within the COMSOL chemical reaction engineering module [121]. Details on the equations presented in this section can be found in the COMSOL User's Guide, unless specified otherwise [121,123].

While our model consists of two global (and thus dimensionless) models, we describe their interaction using a plasma cylinder surrounded by a larger, colder cylinder. There is energy and species exchange between the two zones following an imposed Bessel profile on both the temperature and the species densities. We then calculate the mass and energy exchange through their connecting surface, and this explains why the geometry is important to include here in this section. Figure 2-3(a) illustrates the simulation domain with the exchange surface and its dimensions. The dimensions of these domains are based on the experimental setup, presented in Figure 2-3(b) and described in more detail by Fontaine et al. [124]. We use a 2 mm electrode gap, which is the set height of both cylinders. A plasma radius of 0.25 mm was found to yield the best agreement with experimental results for both product selectivity and the H/CH and C₂/CH intensity ratios, as measured by optical emission spectroscopy, as discussed in detail by Fontaine et al. [124].

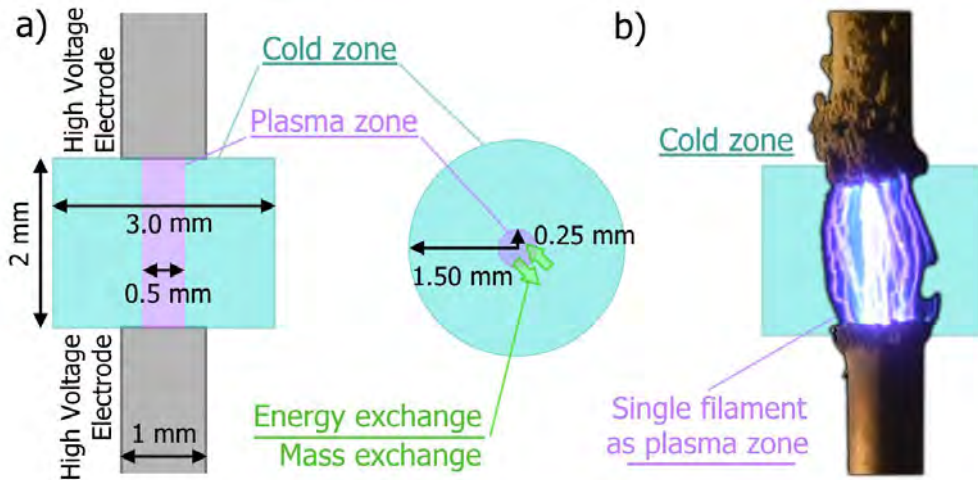


Figure 2-3 - Schematic illustration of the two-zone simulation domain (a) and of the experimental setup with an image of 20 pulses (b). The plasma zone is indicated in purple, with a radius of 0.25 mm. The cold surrounding zone is indicated in light blue with an initial radius of 1.50 mm (which can expand during the simulation). The energy and mass exchange between both zones is represented by the green arrows.

In the next sections, we explain the governing equations, which are split into the plasma model (2.5.4), the cold zone model (2.5.5), and the energy and mass exchange between the two zones (2.5.6). Domain-specific variables are denoted with subscript p for plasma and subscript c for cold zone. Finally, in section 2.5.7, we will discuss the advantages and limitations of this new modeling approach.

2.5.4 Global plasma model equations

The plasma zone is fixed by the plasma radius and determined from our experiments [124]. This means that the plasma volume is constant, so the pressure must vary to account for increases or decreases in species densities due to rising temperature and dissociative chemical reactions. The pressure is determined from the conservation of total mass, detailed in section 2.5.6. The governing equations in the plasma zone are the heavy-species energy balance, the electron energy balance, the heavy-species mass balance, and several vibrational-temperature balance equations. Equation 65 presents the heavy species energy balance, based on the heavy species energy balance in the plasma module and the energy balance for a continuously stirred tank reactor (CSTR) in COMSOL:

$$C_{p,p}\rho_p \frac{dT_{g,p}}{dt} = - \sum_j H_j r_j + \sum_{j,elastic} S_{el,j} + \sum_{j,e-diss} h_{add,j} r_j + \frac{dp_p}{dt} - \frac{8\lambda_p}{\Lambda_L^2} (T_{g,p} - T_{g,c}) - \sum_i (h_{i,p} - h_{i,c}) \varphi_{i,p} \quad [65]$$

Here, $C_{p,p}$ is the heat capacity of the gas at constant pressure ($\text{J.kg}^{-1}.\text{K}^{-1}$), ρ_p is the gas density (kg.m^{-3}), $T_{g,p}$ is the gas temperature (K), H_j is the enthalpy of reaction j (J.mol^{-1}), r_j is the reaction rate of reaction j ($\text{mol.m}^{-3}.\text{s}^{-1}$), $S_{el,j}$ is the energy to heavy species from elastic collisions of reaction j as described by Hagelaar et al. [90] (W.m^{-3}), $j, e - diss$ is referring to all reactions involving electron-impact dissociation, $h_{add,j}$ is the additional energy difference between the predissociation state and the dissociation products of reaction j (J.mol^{-1}), p is the pressure (Pa), λ_p is the mixture thermal conductivity ($\text{W.m}^{-1}.\text{K}^{-1}$), Λ_L is the Bessel-corrected plasma radius (m), $T_{g,c}$ is the gas temperature of the cold zone (K), $h_{i,p}$ and $h_{i,c}$ are the specific enthalpy of species i in the plasma and cold zone, respectively (J.kg^{-1}), and $\varphi_{i,p}$ is the density gain of species i from the cold zone to the plasma zone ($\text{kg.s}^{-1}.\text{m}^{-3}$).

The left-hand side of the equation describes the change of energy to the gas. Only the gas temperature is differentiated with respect to time, since the last term on the right-hand side of the equation accounts for the heating of the inflowing gas. The first term on the right-hand side describes the heat lost or gained due to chemical reactions. The molar enthalpy for individual species is determined from the 7-term NASA polynomials of Burcat et al. [102]. The rates of all thermal reactions are obtained from rate coefficients (k_{th} in $\text{m}^3.\text{mol}^{-1}.\text{s}^{-1}$ or $\text{m}^6.\text{mol}^{-2}.\text{s}^{-1}$, depending on the reaction order), which

depend on the gas temperature, following the Arrhenius equation (equation 2) or a pressure-dependent form of it, like fall-off functions.

In addition to this equation, the global plasma model solves the equations in section 2.5.1 and several vibrational-temperature balance equations for CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , and H_2 . However, they do not contribute to the chemistry and serve only as a small energy reservoir. The following modes are considered in the model:

For CH_4 : $\text{CH}_4(\text{v}2, \text{v}4)$ and $\text{CH}_4(\text{v}1, \text{v}3)$;

for C_2H_2 : $\text{C}_2\text{H}_2(\text{v}5)$, $\text{C}_2\text{H}_2(\text{v}2)$ and $\text{C}_2\text{H}_2(\text{v}3, \text{v}1)$;

for C_2H_4 : $\text{C}_2\text{H}_4(\text{v}1)$ and $\text{C}_2\text{H}_4(\text{v}2)$;

for C_2H_6 : $\text{C}_2\text{H}_6(\text{v}2, \text{v}4)$ and $\text{C}_2\text{H}_6(\text{v}1, \text{v}3)$.

These modes are considered independently of each other. A CH_4 species can be in the first level of both $\text{v}2, \text{v}4$, and $\text{v}1, \text{v}3$ at the same time. These modes can only act as an energy reservoir, and no changes in reaction rates are induced by this vibrational excitation, as it has little to no effect on CH_4 , consistent with previous work [71,125].

For H_2 , the first 14 levels are resolved, assuming a Boltzmann distribution at their respective vibrational temperatures. Electron-impact and thermal reactions affect this vibrational temperature and release or take heat as any reaction would. This approach has been taken from previous work in the literature [95,98].

This storage of vibrational energy has little to no effect on the gas temperature profile. Indeed, at most, the vibrational modes account for 10% of the deposited energy, releasing it a few nanoseconds later, and this does not significantly affect the temperature profile. The relaxation is so fast that the energy is never stored until after the pulse; hence, the electron-to-gas-temperature transition via vibrational modes might as well be considered in one step. Therefore, the vibrational temperatures will not be discussed in Chapter 6.

2.5.5 Global cold model equations

Unlike the global plasma model, the global cold model assumes a constant pressure of 1 atm, as it can occupy the entire reactor body; therefore, the production of additional chemical species through reactions results in an expansion of the cold volume. We consider an initial radius of 1.50 mm, ensuring that the cold volume contains sufficient cold gas to cool the hot plasma after the pulses; however, this radius is subject to change

during the simulation. However, as with the pressure in the global plasma model, the change in this volume is not governed by an equation in the cold zone. Instead, it follows the conservation of total mass, detailed in section 2.5.6. The governing equations in the cold zone are the heavy-species energy and mass balance equations. No electrons or ions are present in the cold zone; hence, we do not solve an electron energy balance equation. Equation 66 describes the heavy species energy balance of the cold zone, based on the equation for a CSTR at constant pressure from the COMSOL reaction engineering module:

$$C_{p,c}\rho_c \frac{dT_{g,c}}{dt} = - \sum_j H_j r_j + \frac{8\lambda_p}{\Lambda_L^2} (T_{g,p} - T_{g,c}) + \sum_i (h_{i,p} - h_{i,c}) \varphi_{i,c} + \sum_{i,ion} (h_{i,ion} - h_{i,neutral}) \varphi_{i,ion-c} \quad [66]$$

Here, all symbols are the same as for equation 65, but with subscripts changed from p to c , to indicate the cold zone instead of the plasma zone, $\varphi_{i,c}$ is the density gain of species i from the plasma zone to the cold zone ($\text{kg.s}^{-1}.\text{m}^{-3}$), $h_{i,ion}$ is the enthalpy of ion i (J.kg^{-1}), $h_{i,neutral}$ is the respective neutral species of the ion i , dissociated if needed (J.kg^{-1}) and $\varphi_{i,ion-c}$ is the density gain from the plasma to the cold zone for ion i ($\text{kg.s}^{-1}.\text{m}^{-3}$), resulting from ion-electron recombination in the cold zone, as no ions and electrons can survive here (without electric field or high gas temperature).

The left-hand side of the equation again represents the change in the system's energy, with all source terms on the right-hand side. The first right-hand side term is again the heat lost or gained from chemical reactions, and the second term (thermal conduction) is the opposite of the thermal conduction term of equation 65. The third term is the heat released by species entering the cold zone from the plasma zone. As the temperature is uniform, all species entering the cold zone from the plasma zone instantly relax to the cold zone temperature and release the enthalpy difference as heat. Finally, the last term is the energy released from ion recombination. When an ion enters the cold zone, it immediately recombines with an electron (linked by equation 59) and releases the recombination energy to the cold zone. Ions that do not have a stable neutral state by just recombining with an electron will dissociate upon recombination into stable neutrals.

Like in the plasma zone, all reaction rate coefficients (thermal in this case) follow a form of the Arrhenius equation (equation 2).

2.5.6 Energy and mass exchange equations between zones

As mentioned in both sections 2.5.4 and 2.5.5, we use a total mass balance to obtain the change in pressure in the plasma zone and the change in volume of the cold zone; the loss of mass in one zone must equal the gain in the other. This mass change follows:

$$\frac{dm_p}{dt} + J_{p,out} + F_{p,out} = 0 \quad [67]$$

$$\frac{dm_c}{dt} = \frac{-dm_p}{dt} \quad [68]$$

Here, m_p and m_c are the masses of the plasma and cold zone, respectively (kg), $J_{p,out}$ is the mass loss due to diffusion out of plasma zone (kg.s^{-1}) and $F_{p,out}$ is the mass loss due to pressure-enforced flow out of plasma zone (kg.s^{-1}).

The total diffusive molar outflow from the plasma, $J_{p,out}$, is defined by equation 69, again assuming a Bessel profile. Note that we assume diffusion of all species into the cold zone, assumed to be composed of CH_4 almost exclusively, as the volume of the cold zone is much larger than the plasma zone, meaning strong dilution. The total mass loss via diffusion is described by the following equation.

$$J_{p,out} = \sum_i \left[\frac{D_{i,\text{CH}_4}}{\Lambda_L^2} (c_{p,i} - c_{c,i}) V_p - x_{i,c} \sum_j \frac{D_{j,\text{CH}_4}}{\Lambda_L^2} (c_{p,j} - c_{c,j}) V_p \right] M_{p,n} \quad [69]$$

Here D_{i,CH_4} is the binary diffusion coefficient of species i and CH_4 ($\text{m}^2.\text{s}^{-1}$), $c_{p,i}$ is the molar concentration of species i in the plasma zone (mol.m^{-3}) and $c_{c,i}$ is the molar concentration of species i in the cold zone (zero for ions, mol.m^{-3}), V_p is the plasma volume (m^3), $x_{i,c}$ is the molar fraction of species i in the cold zone (unitless) and $M_{p,n}$ is the mean molar mass in the plasma zone (kg.mol^{-1}). The ordinary diffusion equations should not yield pressure differences between both zones. Hence, diffusion from the cold zone to the plasma zone is considered to be particle-for-particle [126]. This leads to a correction term, shown as the second term in the summation over species i . The mass loss for a species i is equal to equation 69 without taking the overarching sum and multiplying by the molar mass of species i . The binary diffusion coefficient is calculated using the Chapman-Enskog approach, following equation 70 [127]:

$$D_{i,j} = 2.66 \times 10^{-22} \frac{\sqrt{T^3 \left(\frac{1}{M_i} + \frac{1}{M_j} \right)}}{p \sigma_{ij}^2 \Omega_{D,ij}} \quad [70]$$

Here, M_i and M_j are the molar mass of species i and j , respectively (kg.mol^{-1}), p is the total pressure (Pa), σ_{ij} is the collision diameter of species i and j (m) and $\Omega_{D,ij}$ is the dimensionless collision integral of species i and j , given by equation 71 [127].

$$\Omega_{D,ij}(T^*) = \frac{1.06036}{T^{*0.1561}} + 0.193e^{-0.476357T^*} + 1.036e^{-1.52996T^*} + 1.765e^{-3.894117T^*} \quad [71]$$

$$T^* = \frac{T}{\sqrt{\epsilon_i \epsilon_j} / k_B} \quad [72]$$

Here, ϵ_i and ϵ_j are the potential energy minima of species i and j , respectively (K), and k_B is the Boltzmann constant.

The equations for pressure-enforced mass exchange describe the flow as a gain term, going from a high-pressure region to a low-pressure region [128]. Furthermore, we distinguish between choked and non-choked flow, defining choked flow as occurring when the Mach number exceeds unity. The Mach number is calculated as follows:

$$M_c = \sqrt{\frac{2}{\gamma - 1} \left[\left(\frac{p_h}{p_l} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]} \quad [73]$$

$$\gamma = \frac{C_p M_n}{C_p M_n - R_g} \quad [74]$$

Here, p_h and p_l are the high and low pressures, respectively (Pa). Both the plasma and cold zones can be high-pressure zones, depending on the plasma zone pressure, since the cold zone pressure is set to 1 atm. γ is the ratio of specific heats (C_p/C_v) and is calculated for the high-pressure zone, and R_g is the universal gas constant.

Here we show the equations for flow from a high-pressure to a low-pressure zone, which is $F_{p,out}$ when the plasma zone is at elevated pressure and the negative of it when the plasma zone is at lower pressure. When the system has a Mach number below one, we describe a non-choked mass flow, following equation 75:

$$F_{non-choked} = p_h A \sqrt{\frac{\gamma M_n}{R_g T_{g,h}}} \frac{M_c}{\left(1 + \frac{\gamma-1}{2} M_c^2\right)^{(\gamma+1)/2(\gamma-1)}} \quad [75]$$

Here, A is the connecting area of the two domains (m^2 , here $2\pi r_p h$), $T_{g,h}$ is the gas temperature of the high-pressure zone (K). When the Mach number is equal to or larger than one, this equation becomes a choked mass flow equation:

$$F_{choked} = p_h A \sqrt{\frac{\gamma M_n}{R_g T_{g,h}}} \left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)} \quad [76]$$

The combination of equations 67 and 68, along with the following diffusional and pressure-enforced exchange equations, defines the net mass exchange between the plasma and the cold zone. The energy exchange should therefore also follow a diffusional and pressure-enforced part. The pressure-enforced energy exchange has already been shown in equations 65 and 66. In equation 65, this is the final term on the right-hand side, as the energy needed to heat the incoming cold gas. In equation 66, these are the final two terms on the right-hand side, as the energy deposited by cooling down to the cold temperature and the energy released from ion-electron recombination. The diffusional energy exchange is determined via thermal conductivity. Here, the variable λ_p has not been detailed yet and is shown below. It should be noted that these equations are similar to the mass diffusional equations, as they are indeed closely related.

The last variable to be defined in equation 65 is thus λ_p , i.e., the total thermal conductivity. It is defined as the average of the arithmetic and harmonic mean of the individual species thermal conductivities via equation 77, and the individual thermal conductivity (λ_i) is defined by equation 78, following a similar Chapman-Enskog approach as for diffusion [127]:

$$\lambda_p = 0.5 \left(\sum_i x_i \lambda_i + \left(\sum_i \frac{x_i}{\lambda_i} \right)^{-1} \right) \quad [77]$$

$$\lambda_i = 2.669 \times 10^{-6} \frac{\sqrt{1000 T_g M_i}}{(10^{10} \sigma_i)^2 \Omega_\mu(T^*)} (1.15 C_{p,i} + 0.88 R_g) \quad [78]$$

Here, σ_i is the potential characteristic length (m) and $C_{p,i}$ is the individual species heat capacity ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) obtained from the NASA polynomials as discussed above. The dimensionless collision integral, $\Omega_\mu(T^*)$, is defined as follows [127]:

$$\Omega_\mu(T^*) = \frac{1.16145}{T^{*0.14874}} + 0.525e^{-0.7732T^*} + 2.162e^{-2.43787T^*} + \frac{4.998 \times 10^{-40} \mu_i^4}{(10^{10} \sigma_i)^6 k_B^2 \epsilon_i T} \quad [79]$$

$$T^* = \frac{T}{\epsilon_i/k_B} \quad [80]$$

Here, μ_i is the dipole moment of species i (C.m). All transport parameters used in this work are obtained from the GRI-MECH 3.0 set [122].

2.5.7 Advantages and limitations of the two-zone approach

While this modeling approach is clearly an improvement over temperature-fitted global modeling of ns-pulsed plasmas [71,125] and is thus more self-consistent, it also has clear limitations compared to higher-dimensional modeling of ns-pulsed plasmas, which can describe streamer formation and dynamics.

Indeed, our model cannot describe streamer formation, and for very short pulses (on the order of a few ns), this will affect the local non-thermal chemistry in the streamer head [129]. The latter will affect the plasma radius, which is assumed constant in our model. For this reason, we only describe ns-pulses of 10 ns or more. Multidimensional modeling would also allow us to simulate the plasma transition from streamer to glow and later to a filamentary mode, which, in turn, yields non-uniform gas heating [130]. Such (2D) models, however, are only feasible for a small, validated set of chemical kinetics with a limited number of species [131,132]. Still, they are not feasible for CH_4 ns-pulsed plasmas, as the number of species to consider is far greater than in existing 2D models.

On the other hand, as mentioned above, our modeling approach is already a major step forward compared to existing global models, as we calculate the gas temperature self-consistently by solving the energy balance equation and accounting for the mass and energy exchange between the hot plasma and the cold surrounding zone. Furthermore, the additional conservation-of-mass equation allows us to calculate the pressure in the plasma pulse, which is usually assumed constant in models in the literature [71,125]. This allows comparison with experimental data using only one tunable parameter,

namely the plasma radius, and the value assumed in our model is reasonable, based on experimental images from both the setup under study and previous ns-pulse experiments [71]. Comparison of our model to experimental data shows reasonable agreement, though not quantitative; the latter cannot be expected from a global model. In future work, we plan to perform a sensitivity/reduction analysis to keep only the most important species and provide a small, validated set for 2D modeling, as we do for warm plasma modeling (see section 2.3 above).

Chapter 3

Multidimensional model of dry reforming of methane with oxygen addition in an atmospheric pressure glow discharge

The content of this chapter is in part based on:

Coupled multi-dimensional modelling of warm plasmas: Application and validation for an atmospheric pressure glow discharge in $\text{CO}_2/\text{CH}_4/\text{O}_2$

Maerivoet S.*, Tsonev I.*, Slaets J., Reniers F., Bogaerts A.

Chemical Engineering Journal, 2024, 492, 152006

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and

Effect of O_2 on Plasma-Based Dry Reforming of Methane: Revealing the Optimal Gas Composition via Experiments and Modeling of an Atmospheric Pressure Glow Discharge

Maerivoet S.*, Wanten B.*, De Meyer R., Van Hove M., Van Alphen S., Bogaerts A.

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<https://doi.org/10.1021/acssuschemeng.4c04283>

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To support experimental research into gas conversion by warm plasmas, models should be developed to explain the experimental observations. These models need to describe all physical and chemical plasma properties in a coupled way. In this chapter, we present a modeling approach to solve the complete set of assumed relevant equations, including gas flow, heat balance, and species transport (as explained in the previous chapter), coupled with a rather extensive chemistry set, consisting of 21 species, obtained by reduction of a more detailed chemistry set, consisting of 41 species. We apply this model to study the combined CO_2 and CH_4 conversion in the presence of O_2 , in a direct current atmospheric pressure glow discharge. Our model can predict the experimental trends and can explain why higher O_2 fractions result in higher CH_4 conversion, namely due to the higher gas temperature, rather than just by additional chemical reactions. Indeed, our model predicts that when more O_2 is added, the energy required to reach any set temperature (i.e., the enthalpy) drops, allowing the system to reach higher temperatures with similar amounts of energy. This, in turn, is related to the higher H_2O and lower H_2 fractions formed in the plasma, as demonstrated by our model. Altogether, our new self-consistent model can capture the key physics and chemistry in this warm plasma, which is an important step towards predictive modeling of plasma-based gas conversion.

3.1 Introduction

As explained in Chapter 1, the global modeling approach fails to accurately describe contracted atmospheric plasmas and should be used with caution. In addition, the radial dependence of thermal conductivity on plasma composition makes the problem even more strongly dependent on the gas spatial parameters. When a swirling flow is employed, a 1D approximation also becomes questionable, due to the lack of analytical expressions describing the flow behavior in such systems. To accurately describe the behavior of a plasma and its afterglow in a non-uniform geometry with swirling flow, the system's multidimensionality must be accounted for, along with all relevant physics and chemistry.

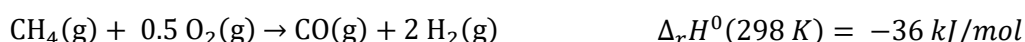
The gas conversion in warm plasmas, e.g., high-current gliding arc (GA), microwave (MW), and atmospheric-pressure glow discharge (APGD) plasmas, is thermally driven [73,74,79,105,133,134]. Even though the gas temperature of these low-current high-voltage plasmas reaches a few thousand Kelvin, the electron temperature is still higher; hence, the plasma is not a thermal plasma. On the other hand, the gas temperature is much higher than for non-thermal plasmas (which are close to room temperature). Therefore, these plasmas are typically called “warm plasmas”. The most important chemistry, which changes the gas composition in a notable, experimentally verifiable way, can be described by a kinetic scheme that depends only on translational temperature and pressure. This allows the chemistry to be realistically described using a thermal kinetics model, excluding the effects of electrons on the gas composition. The electrons in the plasma are still considered for gas heating, which the model describes as a heat source at the position of the plasma core.

The main improvement of our model compared to previous CFD models [73,74,105–107] is that we include the self-consistent computation of the heat capacity and thermal conductivity of the gas mixture/plasma in a 2D swirling flow. Indeed, gas flow velocity and diffusion affect the system's thermodynamic properties, and local chemical equilibrium (LCE), as assumed in previous CFD models, is not reached. By design, this includes solving the full chemistry in the 2D model, which is not the case for the previous CFD models [73,74,105–107]. A comparison with experimental results shows that this modeling approach is necessary to accurately describe the behavior of a real plasma reactor.

As a case study, we apply these coupled models to simulate the effect of O_2 addition on the combined CH_4 and CO_2 conversion in an APGD plasma, the so-called oxidative CO_2

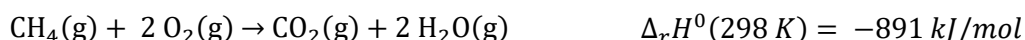
reforming of methane (OCRM), which allows for stable plasma conditions up to large enough CH₄ fractions, without much soot formation, that can be modelled in a stationary manner, with enough variation in chemical composition, to yield interesting results and obtain the most thorough model validation. These coupled models allow us to obtain otherwise unknown parameters, e.g., temperature and species density profiles, as well as reaction pathways as a function of position in the plasma reactors, which can all help to gain more insight in the underlying mechanisms, and to explain the experimental trends.

The addition of O₂ to CH₄ and CO₂ plasmas would allow for the partial oxidation of CH₄:



to assist in the conversion of CH₄ besides the dry reforming of CH₄ (DRM), discussed in Chapter 1.

In addition, some other reactions will take place, resulting in (undesired) side-products (e.g., H₂O), such as the reverse water-gas shift, as seen in Chapter 1, and the full oxidation of CH₄:



These reactions would obviously suggest a higher conversion of CH₄ (and CO₂) upon addition of O₂. However, our model indicates that the reality is more complex. Indeed, the large endothermicity of DRM and the large exothermicity of the full oxidation of CH₄ strongly affect the plasma temperature, which in turn impacts the thermodynamic equilibria and the kinetics of the system. This explains the need for a detailed, self-consistent multidimensional computational model that fully couples all physics and chemistry.

3.2 Computational and experimental details

The model follows the multidimensional modeling approach explained in Chapter 2. In this section, aside from the experimental details, the specific geometry and boundary conditions will be detailed.

3.2.1 3D geometry and meshing

Figure 3-1 depicts the APGD reactor geometry (left) and the transition to the 3D modeled geometry (middle). We use a tetrahedral mesh, consisting of 18 million elements, including boundary layers, as illustrated in the right picture of Figure 3-1.

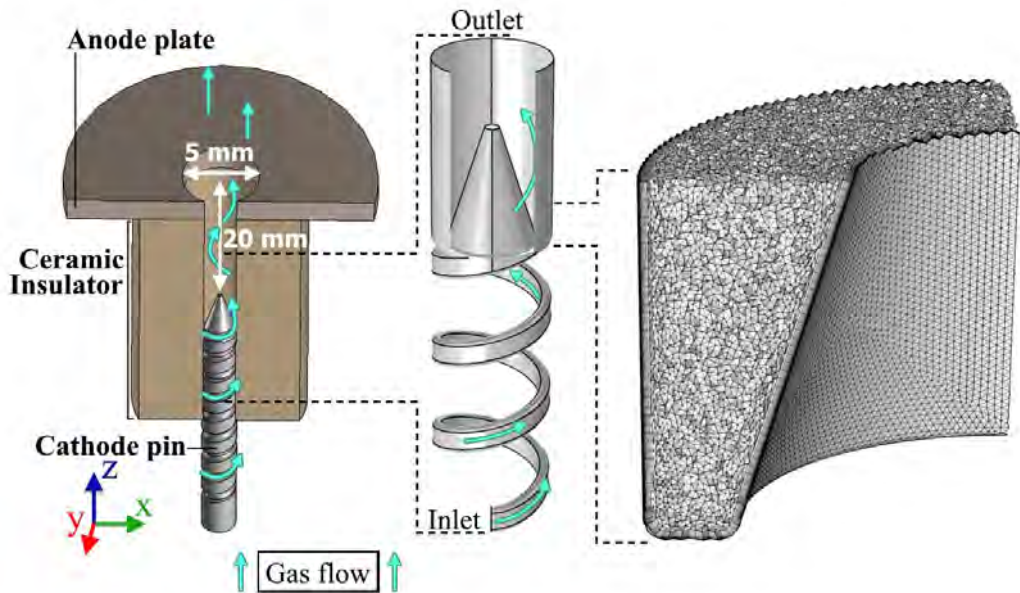


Figure 3-1 - Schematic representation of the atmospheric pressure glow discharge (APGD) reactor (left), the corresponding implementation in the 3D model (middle), and the size of the mesh cells (right). The gas flow is indicated in turquoise.

Understanding the 3D gas flow profile is essential before exploring the 2D axisymmetric model. Indeed, the inlet of the coupled 2D axisymmetric model should not have a negative mass flow at any point. To avoid this, we first studied the inlet flow profile using a 3D fluid dynamics model that includes only the fluid flow equations (see Chapter 2, section 2.4.1 above).

3.2.2 2D inlet gas velocity profile

The velocity profile in the APGD arises from the flow profile in the cathode pin groove. As just the tip of the cathode is considered in the 2D model and the extended groove is omitted, the 2D inlet velocity profile should resemble the flow profile at the corresponding position in the 3D model. The left side of Figure 3-2 shows the xz -projection of the 3D model, with a red line indicating the location where the velocity profiles are transferred to the 2D axisymmetric model. The right side shows the cut plane

at this position, from which the velocity in cylindrical coordinates can be obtained as a function of the radius. We take the average velocity value in three cylindrical coordinates (r, φ, z) of 130 circles with radii ranging from 1.85 mm to 2.5 mm, to obtain the 2D axisymmetric inlet velocity profile.

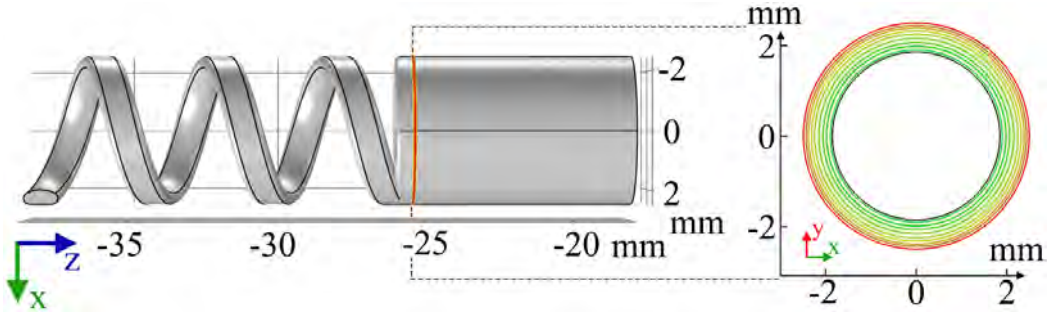


Figure 3-2 - Translation of a cut plane in the 3D flow model to the inlet boundary condition of the 2D axisymmetric model.

3.2.3 2D geometry and boundary conditions

Figure 3-3 depicts the setup of the axisymmetric 2D model. The post-plasma region, as shown on the left of the figure, is included in the axisymmetric simulation, extending the domain to 89 mm in the z direction. An inlet velocity field is defined, as obtained from the 3D model, described in section 3.2.2 above. The outlet at the end suppresses backflow, while all walls have a no-slip condition. A heat source is defined above the cathode pin, following the shape measured by Trenchev et al. [135]. Two different heat transfer coefficients, h , are defined for the different materials at the walls: glass and ceramic walls are described with $h = 5 \text{ W}/(\text{m}^2\text{K})$ (indicated in purple in Figure 3-3), while $h = 25 \text{ W}/(\text{m}^2\text{K})$ is used for stainless steel (both cathode pin and anode plate; indicated in green) [136].

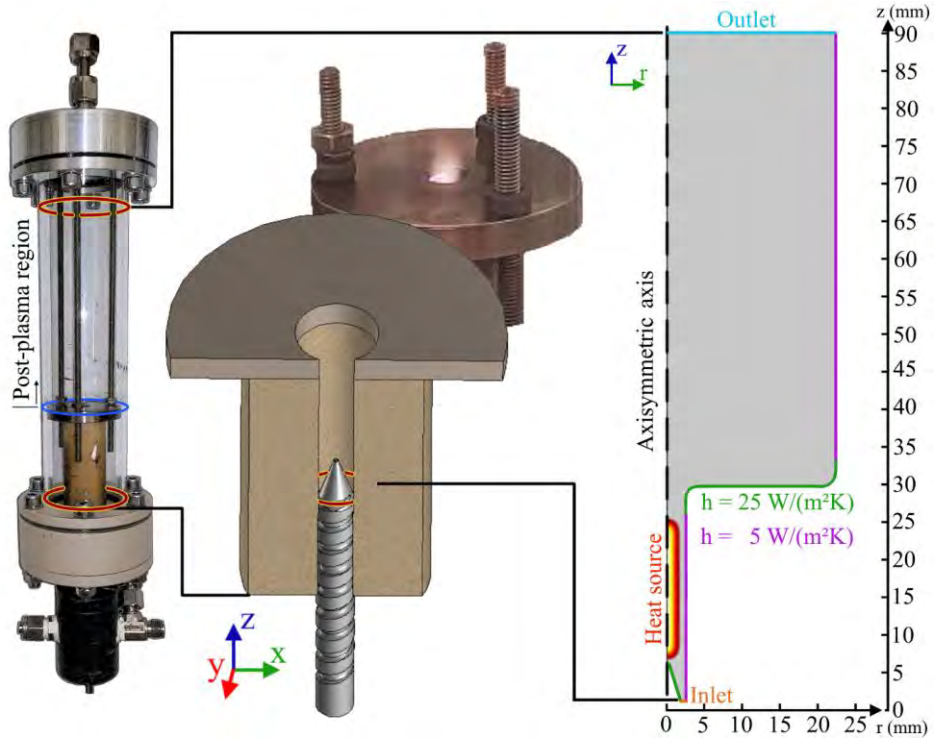


Figure 3-3 - Picture of the APGD (left), with detail of the schematic plasma reactor and plasma afterglow image (middle), and translation to the axisymmetric 2D model (right). Boundaries marked on the 2D scheme include: outlet, inlet, two heat transfer coefficients (one for anode steel and one for ceramics and glass), and the heat source.

The heat source is described using a Gaussian profile in the radial direction and a rectangular profile in the axial direction, as shown in Figure 3-4. This means that the current conservation equations of Chapter 2 (section 2.4.4) are not solved. Indeed, this heat source acts as the Joule heating of the electrons to the gas and provides a set power to the model, dependent on the area under the function curves. This value is multiplied by a constant to reach the desired input power. The shape of the heat source, as measured by Trenchev et al. [135], is determined for a CO_2 plasma rather than a $\text{CO}_2/\text{CH}_4/\text{O}_2$ plasma; hence, there might be a small difference in the radial profile of the plasma. Nevertheless, we chose not to adjust the plasma radial profile to better fit the experimental results, as this would give the unfair impression that our model can predict the exact conversion, even though it would be achieved by fitting the heat-source shape, which might be unphysical. We prefer to claim that we can predict experimental trends across conditions using a purely physical model without any fitting parameters, and to gain insights from results with experimental justification.

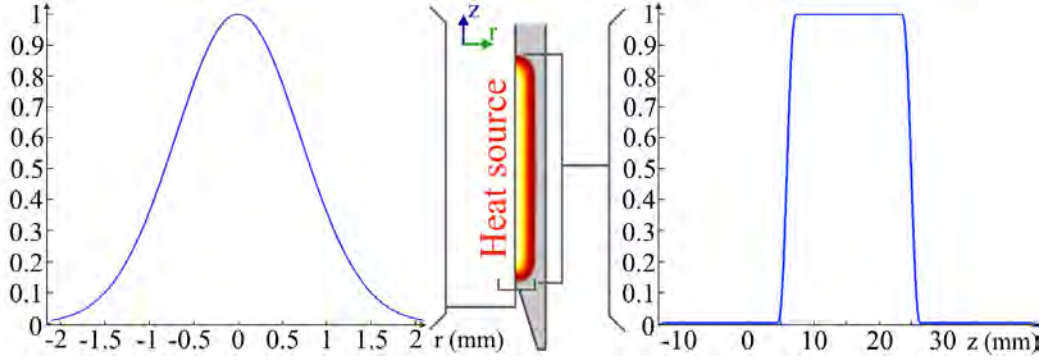
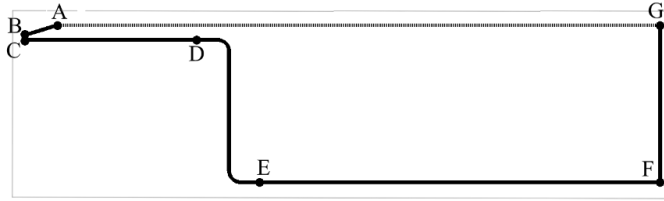


Figure 3-4 - Description of the heat source, using a Gauss function radially and a smoothed rectangle axially.

The boundary conditions for the SST RANS equations are listed in Table 3-1 [110]. $\mathbf{u}_0$ is the inlet velocity field, $\mathbf{u}|_{l_w=0}$ is the velocity at the wall, $\hat{p}_0$ is the outlet pressure, I_T is the turbulent intensity, U_{ref} is the reference velocity magnitude, L_T is the turbulent length scale, β_0^* is 0.09, a turbulence model parameter, ω_{visc}^2 and ω_{log}^2 are the specific dissipation values for the linear sublayer and logarithmic layers, respectively, $\mathbf{n}$ is the normal vector to the boundary plane, $h_\perp$ is the reference length and l_w is the closest wall distance.

Table 3-1 - Boundary conditions for the SST RANS (flow) equations [110]

Geometry



	p (Pa)	$\mathbf{u}$ (m/s)	k (m ² /s ²)	ω (1/s)
<i>Inlet</i> BC	/	$\mathbf{u} = \mathbf{u}_0$	$k = \frac{3}{2} (U_{ref} I_T)^2$ $U_{ref} = \ \mathbf{u}_0\ $	$\omega = \frac{k^{0.5}}{(\beta_0^*)^{0.25} L_T}$
<i>Walls</i> AB & CF	/	$\mathbf{u} _{l_w=0} = \mathbf{0}$ $l_w = \frac{h_\perp}{2}$	$\nabla k \cdot \mathbf{n} = 0$	$\omega = \sqrt{\omega_{visc}^2 + \omega_{log}^2}$
<i>Outlet</i> FG	$[-pI + K]\mathbf{n} = -\hat{p}_0 \mathbf{n}$	/	$\nabla k \cdot \mathbf{n} = 0$	$\nabla \omega \cdot \mathbf{n} = 0$

The boundary conditions for the heat balance equation are listed in Table 3-2 [120]. Here T_{ustr} is upstream temperature, ΔH is the sensible enthalpy, $\mathbf{q}$ is the heat flux, q_0 is the inward heat flux, T_{ext} is the external temperature and Q_0 is the user-defined heat source.

Table 3-2 - Boundary conditions for the heat balance equation [120]. The geometry describing the mentioned boundaries is depicted in Table 3-1.

	T (K)	$\mathbf{q}$ (W/m ²)	Q (W/m ³)
<i>Inlet</i> BC	$T_{ustr} = 293.15$	$-\mathbf{n} \cdot \mathbf{q} = \rho \Delta H \mathbf{u} \cdot \mathbf{n}$ $\Delta H = \int_{T_{ustr}}^T c_p dT$	/
<i>Walls</i> CD & EF	/	$-\mathbf{n} \cdot \mathbf{q} = q_0$ $q_0 = h(T_{ext} - T)$ $T_{ext} = 293.15 \text{ K}$ $h = 5 \text{ W/m}^2\text{K}$	/
<i>Walls</i> AB & DE	/	$-\mathbf{n} \cdot \mathbf{q} = q_0$ $q_0 = h(T_{ext} - T)$ $T_{ext} = 293.15 \text{ K}$ $h = 25 \text{ W/m}^2\text{K}$	/
<i>Outlet</i> FG	/	$-\mathbf{n} \cdot \mathbf{q} = 0$	/
<i>Domain</i>	/	/	$Q = Q_0$

Finally, the boundary conditions for the transport of species equation are listed in Table 3-3 [121]. Here $\omega_{0,i}$ is the user-defined inlet mass fraction, $\mathbf{j}_i$ is the diffusive flux vector of species i and D_i^m is the mixture-averaged diffusion coefficient.

Table 3-3 - Boundary conditions for the transport of species equations [121]. The geometry describing the mentioned boundaries is depicted in Table 3-1.

	ω_i (-)	J_i (mol/(m ² s))
<i>Inlet</i> BC	$w_i = w_{0,i}$	/
<i>Walls</i> AB & CF	/	$-\mathbf{n} \cdot \mathbf{j}_i = \mathbf{0}$
<i>Outlet</i> FG	$-\mathbf{n} \cdot \rho D_i^m \nabla w_i = 0$	/

3.2.4 Experimental setup and gas composition

We performed experiments to validate our model, specifically for the combined conversion of CH₄ and CO₂, with O₂ addition (so-called oxidative CO₂ reforming of methane, OCRM) in an APGD plasma.

We used the reactor shown on the left side of Figure 3-3; the ceramic piece (also described in section 3.2.3) is made from MACOR. The inflow of gas is controlled using Bronkhorst® (F-201CV) mass flow controllers, drawing from 99.5 % purity © Air Liquide gas cylinders (CO₂, CH₄, and O₂). We analyzed the resulting gas mixture using an Agilent 990 Micro gas chromatograph (μGC), with H₂O being separated using a cold trap, to avoid damaging the equipment. Two channels are used: channel 1 uses a molsieve 5A column and Ar as carrier gas; permanent gases (CO, H₂, and O₂) are separated and measured on this channel. Channel 2 uses a PoraPLOT U column and He as a carrier gas, separating CO₂, C₂H₂, C₂H₄, and C₂H₆ from each other and from the other gases. Both channels use a CP PoraBOND Q as a pre-column. The full experimental setup is shown in Figure 3-5 below.

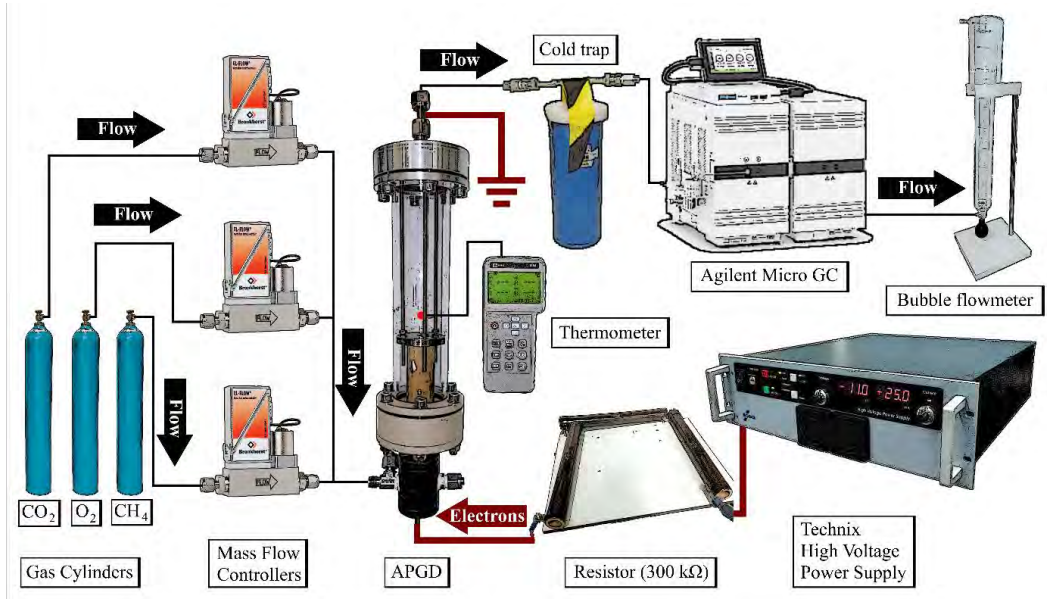


Figure 3-5 - Schematic representation of the entire experimental setup. Black thin lines depict gas flow; red thick lines depict electrical current.

The setup used in these experiments is similar to that investigated by Wanten et al. [137]. Power is supplied to the plasma using a current-controlled Technix HV (SR30KV-1.2KW) power supply. We used a 300 kΩ ballast resistor connected in series with the plasma to stabilize the current going to the discharge. The current during the experiments was kept constant at 25 mA. Due to changes in conductivity across different gas mixtures, the voltage for the same input current varies slightly, which in turn results in a slight difference in deposited power. The plasma power is determined from the voltage and current of the power supply, subtracted by the power into the ballast resistors, as can be seen in equation 81. In our case, as the current was set by the power supply, the voltage was read from the power supply unit for each measurement, i.e., each gas chromatography sample. The voltage given by the power supply is stable in most cases, except for large soot formation cases.

$$P_{\text{plasma}} = V_{\text{supply}} \cdot I_{\text{supply}} - R_{\text{ballast}} I_{\text{supply}}^2 \quad [81]$$

The experimentally investigated gas compositions at the inlet are identical to those in the model, as shown in Table 3-4. The experimental data are obtained from three repetitions of three measurements at each condition.

Table 3-4 - Initial gas composition and plasma power for the experimental conditions to which we applied our model.

Symbol	CO ₂ fraction (%)	CH ₄ fraction (%)	O ₂ fraction (%)	Measured plasma power (W)
α	63	34	3	96.7
β	59	32	9	97.3
γ	55	30	15	92.5
δ	49	36	15	95.0
ϵ	42.5	42.5	15	93.8

In all conditions, we applied a standard total flow rate of 1 L/min and the same input current of 25 mA, resulting in similar plasma power (ranging from 92.5 to 97.3 W). These conditions were chosen as they yield a stable plasma. The plasma becomes unstable when operating with higher than 35 % CH₄ without O₂ and at higher than 43 % CH₄ with 15 % O₂ both due to excessive soot formation.

3.3 Results and discussion

Essentially, we solve three models: a 3D gas-flow model, a 0D full-chemistry model for the chemistry reduction, and a fully coupled 2D axisymmetric model, using input from the other models, as discussed in Chapter 2. Although these models are closely linked, we will first discuss them separately. Therefore, in the following sections, we will discuss the chemistry reduction (section 3.3.1), as well as the 3D flow model (section 3.3.2), before presenting the results of the fully coupled 2D axisymmetric model (sections 3.3.3-3.3.9).

3.3.1 Chemistry reduction

The full and reduced chemistry sets are not shown in this thesis, as this would correspond to 150 extra pages. Therefore, we refer to the supporting information of our paper [138] for all kinetic data. Starting from the full set of 41 species and 734 irreversible reactions, only 21 species and 57 reversible reactions remain after reduction. Figure 3-6 compares this reduced set to the original, full set, by plotting the species molar fractions as a function of time. For clarity, only the molar fractions of the major species (CO₂, H₂O, CO, H₂, CH₄, H, OH, O, and O₂) are plotted; the agreement was similar for all other species. For comparison, the predefined temperature profile used in the calculations is also plotted (black dashed line on the right y-axis). This comparison illustrates that the chemistry reduction was successful.

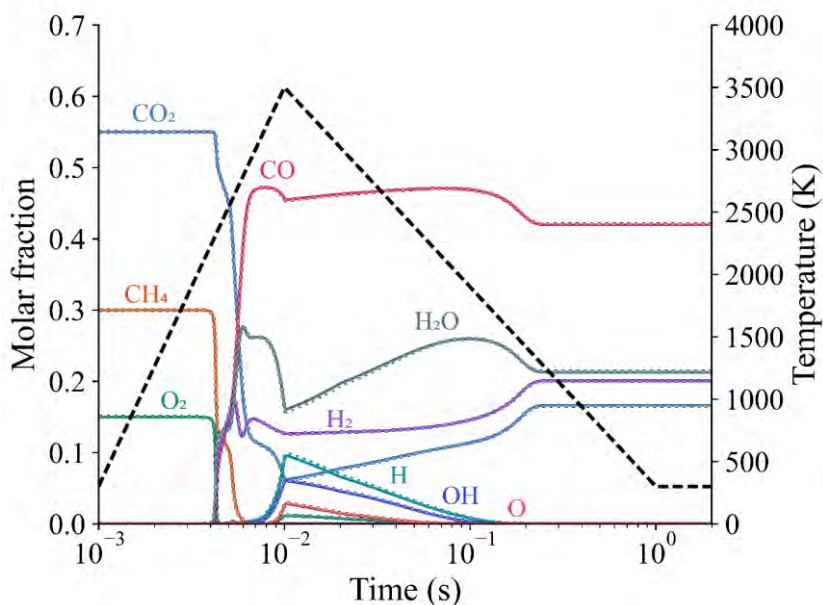


Figure 3-6 - Comparison between the calculated molar fractions of the major species (with fraction above 0.01), calculated with the reduced chemistry set (full lines) and the complete set (dotted lines), as a function of time, for a predefined temperature profile, plotted in black dashed line (right y-axis).

For the reactions, the forward and reverse reactions are paired to reduce computational costs in multidimensional modeling, while reactions without a reverse reaction in the reduced set are paired with the reverse reaction from the full set. This increases the number of reactions a bit, from 87 irreversible to 57 reversible, for a total of 114 reactions. The reduced species set can be found in Table 3-5 below, and the reduced reaction set can be found in Table 3-6, while the corresponding reaction rate coefficients can be found in the supporting information of our paper [138].

Table 3-5 - Reduced set of species, used in the fully coupled 2D axisymmetric model.

Neutral molecules	Radicals
C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂	C ₂ H ₅ , C ₂ H
CH ₄	CH ₃
H ₂	H
CO ₂ , CO	
O ₂	O
CH ₂ O, CH ₂ CO	CHO, CH ₃ O, HCCO
H ₂ O	HO ₂ , OH

Table 3-6 - Reduced set of chemical reactions, used in the fully coupled 2D axisymmetric model. The rate coefficients for all reactions, and the references from which they are adopted, can be found in the supporting information of our paper [138].

$\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$	$\text{CH}_3 + \text{H} \rightleftharpoons \text{CH}_4$	$\text{C}_2\text{H}_6 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_4$
$\text{CH}_3 + \text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_6 + \text{H}$	$\text{CH}_3 + \text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}_2$	$\text{C}_2\text{H}_2 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H} + \text{CH}_4$
$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_6$	$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}$	$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}$
$\text{C}_2\text{H}_5 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6 + \text{H}$	$\text{C}_2\text{H}_2 + \text{H} \rightleftharpoons \text{C}_2\text{H} + \text{H}_2$	$\text{C}_2\text{H}_5 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}$
$\text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2$	$\text{C}_2\text{H} + \text{H} \rightleftharpoons \text{C}_2\text{H}_2$	$\text{M} + \text{CO}_2 \rightleftharpoons \text{M} + \text{CO} + \text{O}$
$\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH}$	$\text{M} + \text{CO} + \text{H} \rightleftharpoons \text{M} + \text{HCO}$	$\text{M} + \text{H} + \text{O}_2 \rightleftharpoons \text{M} + \text{HO}_2$
$\text{CH}_4 + \text{O}_2 \rightleftharpoons \text{CH}_3 + \text{HO}_2$	$\text{CH}_3 + \text{O} \rightleftharpoons \text{H} + \text{HCHO}$	$\text{CH}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{OH}$
$\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{HCHO} + \text{OH}$	$\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{O}$	$\text{CH}_3 + \text{O} \rightleftharpoons \text{CO} + \text{H}_2 + \text{H}$
$\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{OH}$	$\text{H} + \text{HCO} \rightleftharpoons \text{CO} + \text{H}_2$	$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$
$\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$	$\text{CH}_3 + \text{HCO} \rightleftharpoons \text{CH}_4 + \text{CO}$	$\text{HCHO} + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HCO}$
$\text{C}_2\text{H}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{HCHO}$	$\text{C}_2\text{H}_2 + \text{OH} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}$	$\text{CH}_3 + \text{HCHO} \rightleftharpoons \text{CH}_4 + \text{HCO}$
$\text{C}_2\text{H}_4 + \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2$	$\text{C}_2\text{H}_2 + \text{O} \rightleftharpoons \text{H} + \text{HCCO}$	$\text{C}_2\text{H}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{HCO}$
$\text{HCCO} + \text{O} \rightleftharpoons \text{CO} + \text{CO} + \text{H}$	$\text{CH}_2\text{CO} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{CO}$	$\text{CH}_2\text{CO} + \text{H} \rightleftharpoons \text{CH}_3 + \text{CO}$
$\text{M} + \text{HCHO} \rightleftharpoons \text{M} + \text{CO} + \text{H}_2$	$\text{H} + \text{HCHO} \rightleftharpoons \text{CH}_3\text{O}$	$\text{M} + \text{HCHO} \rightleftharpoons \text{M} + \text{H} + \text{HCO}$
$\text{HCO} + \text{OH} \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	$\text{HCO} + \text{HCO} \rightleftharpoons \text{CO} + \text{HCHO}$	$\text{CH}_3\text{O} + \text{CO} \rightleftharpoons \text{CH}_3 + \text{CO}_2$
$\text{CH}_2\text{CO} + \text{OH} \rightleftharpoons \text{CH}_3 + \text{CO}_2$	$\text{CH}_2\text{CO} + \text{CH}_3 \rightleftharpoons \text{CH}_4 + \text{HCCO}$	$\text{CH}_2\text{CO} + \text{H} \rightleftharpoons \text{H}_2 + \text{HCCO}$

The small deviation in the reduced set is due to the strict deviation margin of 0.01 imposed during the reduction process. Across all calculated temperature ranges, only 11 species have molar fractions above 0.01, and Figure 3-6 shows only nine species for this temperature profile. However, the set cannot be reduced to fewer than 21 species because the other species serve as important intermediates in the product composition. These extra (12) species include HO_2 , five species originating from the reaction of CH_4 and O_2 , i.e. HCHO , CH_3O , HCO , CH_2CO , HCCO , and six resulting from the CH_4 chemistry, i.e. C_2H , C_2H_2 , C_2H_4 , C_2H_5 , C_2H_6 and CH_3 . Including the nine species in Figure 3-6, we get a total of 21 species, as listed in Table 3-5 above.

3.3.2 3D RANS SST flow model

Figure 3-7(a) shows the streamlines of the 3D RANS SST flow simulation, while Figure 3-7(b), Figure 3-7(c), and Figure 3-7(d) illustrate the r , φ and z components of the velocity, as calculated with the coordinate translation equations of Chapter 2. As a result

of the nearly tangential gas input, a swirling flow is initiated within the reactor chamber. The swirling flow creates a small pressure gradient, resulting in backflow in the middle of the reactor. [139] Figure 3-7(a) and Figure 3-7(d) show clear backflow from the open boundary, as seen by the negative v_z in Figure 3-7(d). As mentioned in section 3.2.2, the mass flow at the inlet cannot be negative at any position of the 2D inlet, as this would mean that any reacted mass can flow back into the inlet and return as the unreacted inlet mixture, because mass is conserved. The cut plane is shown in Figure 3-7 as a light purple line at a height of 12.5 mm.

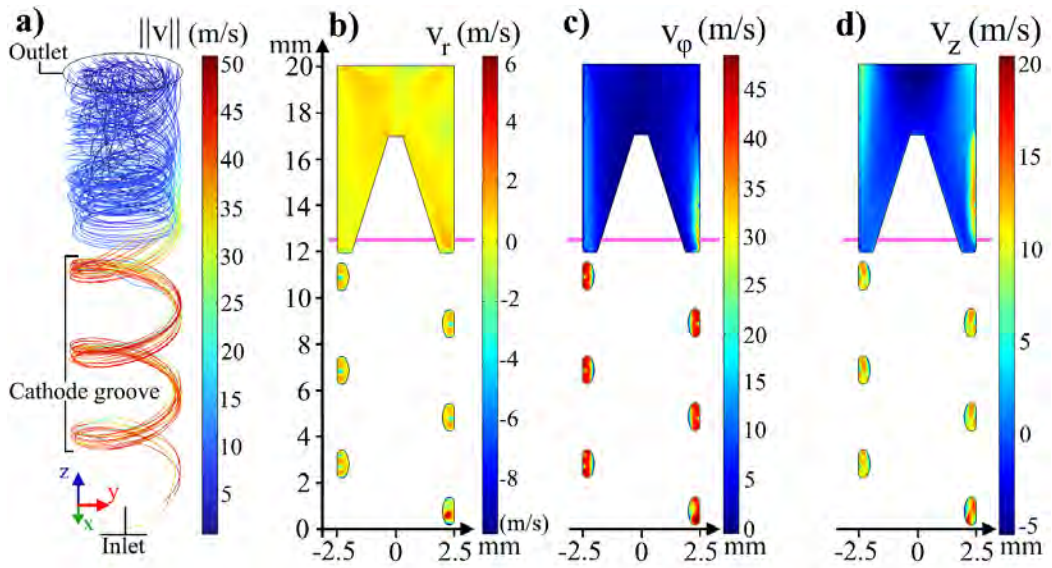


Figure 3-7 - Streamlines calculated with the 3D gas flow model, plotting the velocity magnitude and direction in 3D (a), and three cut-plane plots depicting the r , ϕ and z velocity (b, c, d).

The r component of the velocity is small compared to the other components, reaching a maximum of 6.1 and -9.0 m/s, both at the inlet, but with overall values between 1.0 and -1.0 m/s after the inlet cut plane. The ϕ and z components, on the other hand, are much larger, with ϕ reaching up to 47.9 m/s in the cathode groove. Both show only partial axisymmetric flow, as the magnitude of the velocities is the greatest near the single entrance of the swirling groove flowing into the upper reactor volume. Indeed, the z velocity reaches 19.1 m/s at a single point over the cut plane, while being only 0.2 m/s at the opposing site on the cut plane. This indicates that the 2D axisymmetric approach is not perfect, due to the single gas inlet. Reactors with multiple gas inlets, or entrance points, into the symmetric reactor volume are better suited for this approach. Unfortunately, calculating complex plasma-chemical systems in 3D is currently

computationally unfeasible, and the chemistry really must be included for realistic simulations, so the axisymmetric model is the only feasible option.

3.3.3 Comparison of 2D model and experimental results

First, to validate our model, we compare the calculated CO₂ and CH₄ conversions and the product composition obtained from the coupled model with the experimental data at exactly the same conditions. The conversion of species i in the model, $\chi_{i,model}$, and in the experiments, $\chi_{i,experiment}$, are calculated via equations 82 and 83, respectively:

$$\chi_{i,model} = \frac{n_{i,influent} - n_{i,effluent}}{n_{i,influent}} \quad [82]$$

$$\chi_{i,experiment} = \frac{c_{i,influent} - \alpha \times c_{i,effluent}}{c_{i,influent}} \quad [83]$$

Where n_i is the molar flow rate of species i , c_i is the concentration of species i and α is the gas expansion factor, as described by Wanten et al. [140]. Figure 3-8 depicts the CO₂ and CH₄ conversion for all conditions of Table 3-4. The calculated conversion is evaluated at the outlet of the simulation (i.e., at 89 mm), as shown on the right side of Figure 3-3.

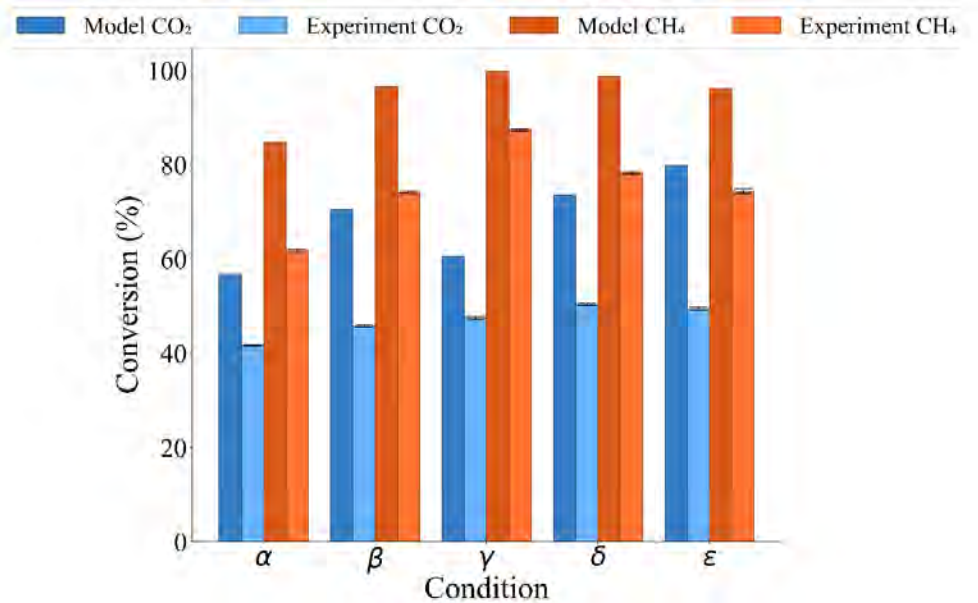


Figure 3-8 - Calculated and experimental CO₂ and CH₄ conversions, for all conditions of Table 3-4. The calculated conversion is evaluated at the outlet of the simulation (at 89 mm), as shown on the right side of

Figure 3-3. The error bars in the experimental data are obtained from three repetitions of three measurements at each condition with great reproducibility.

It is clear that the model overestimates both CO₂ and CH₄ conversion, indicating that some complexities in the experiments (e.g., flow turbulence, effect of details in the reactor geometry, chemistry, ...) are not yet captured by our model. Furthermore, as mentioned in section 3.2.3, some deviation in conversion is likely due to the estimated heat source shape. This heat source was determined before any simulation result was known and has not been changed, to avoid any fitting in this model, as the latter might give the false impression that our model can already predict the absolute conversion at a single condition, while we aim to predict trends with a pure physical model, without any fitting parameter.

When we look at conversion trends across the conditions, we see that the modeled CH₄ conversion trend accurately reflects the experimental trend. Indeed, upon rising O₂ fraction in the mixture (condition α , β and γ), we observe an increase in CH₄ conversion, peaking at condition γ (i.e., 15% O₂), followed by a drop in CH₄ conversion for conditions δ and ϵ (same O₂ fraction of 15%, but rising CH₄ fraction). The lowest CH₄ conversion was observed under condition α in both the experimental and modeled conditions. This is also the case for the CO₂ conversion. However, the calculated CO₂ conversion trends do not perfectly match the experimental trends. The experimental CO₂ conversion does not vary significantly across the various conditions, whereas the calculated CO₂ conversion shows a clear variation. This discrepancy, as well as the correct CH₄ trend and the correct trend of CO₂ conversion between conditions α and β , can be explained by the calculated plasma species analysis, to be presented in section 3.3.5.

Figure 3-9 depicts the composition at the outlet (i.e., at 89 mm) for both the model and the experiment across all conditions in Table 3-4.

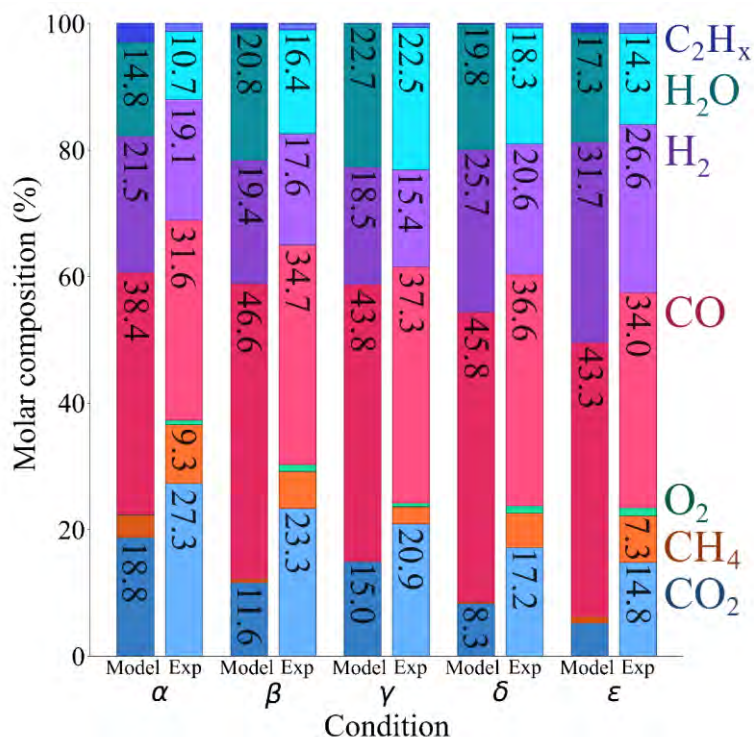


Figure 3-9 - Calculated and experimental molar compositions for all conditions of Table 3-4. The calculated molar composition is evaluated at the outlet of the simulation (89 mm), as shown on the right side of Figure 3-3.

In line with the trend in the conversion plot, the calculated CO₂ fraction shows a mismatch with the experimental data, particularly for the β and γ conditions. Likewise, the trend of CO molar fraction, increasing for both the model and the experiments from the α to β condition, is not found when moving toward condition γ. The trends found in the calculated H₂O and H₂ molar fractions, however, align well with the experimental trends. H₂O reaches a maximum at condition γ, both in the model and experiments, while H₂ shows the opposite trend (again in the model and experiments), reaching a minimum for condition γ.

In general, reasonable agreement is reached between the model and experiments for both conversion and product composition, at least for the trends, while keeping in mind the complexity of the model and the experiments (including the chemistry), and noting that no fitting was used in our model. A setup that would allow more optical diagnostics could enable more complete validation of the model by measuring the densities and

evolution of transient species. For instance, this could include the measurement of the absolute density of the hydrogen atom in the ground state using TALIF, as done by Huang et al. [141]. This will be considered in future work.

The conversion trends also align with thermodynamic expectations, given the overall reactions described in Chapter 1. However, increasing the CH₄ fraction in conditions δ and even further in ϵ would thermodynamically favor the full oxidation of CH₄, resulting in more CO₂ and H₂O formation. This is not the case, as evidenced by both the model and the experiment. This means that the reality is more complex than simple thermodynamic expectations, and we can use our detailed model to explain the experimental trends. For this purpose, we first consider the simplest explanation: a change in temperature.

3.3.4 Temperature and thermodynamic analysis

Figure 3-10 depicts the spatial temperature profiles for all conditions of Table 3-4. The maximum calculated temperature is written for every condition and is located near the anode plate ($z = 25$ mm), as most reactions have taken place before this point.

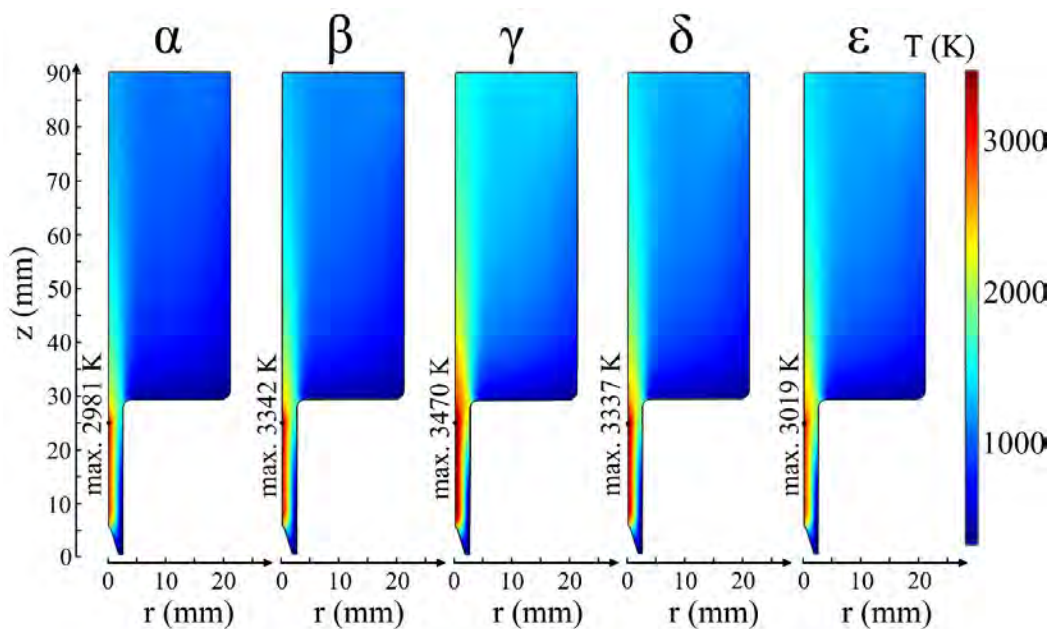


Figure 3-10 - Axisymmetric 2D temperature profiles for all conditions of Table 3-4.

Unfortunately, we were unable to measure the plasma temperature in our APGD reactor. Indeed, we could not use a thermocouple, as it would melt. We performed some

tests with a thermocouple a few millimeters after the plasma, where it already reached 1000 K, but closer to the plasma, or inside the plasma, was not possible; see Figure 3-5. Likewise, we could not apply OES because our APGD reactor is made of ceramic. However, a previous study by Deng et al. [142] has shown that the temperature of an atmospheric-pressure direct-current plasma in the glow regime is approximately 3000 K for dry air. While the temperature will be somewhat different due to the different gas mixture and slightly different operating conditions, this data shows that our calculated temperatures are in the correct order of magnitude.

The increase in CH_4 conversion with rising O_2 fraction in the mixture (Figure 3-8) can be directly linked to the increase in temperature from condition α to γ , as the maximum temperature rises from 2981 K to 3470 K. The decrease in CH_4 conversion with a higher CH_4 fraction in the mixture (also see Figure 3-8) coincides with a drop in temperature from condition γ to ϵ (as the maximum temperature decreases from 3470 K to 3019 K). Hence, it demonstrates that the CH_4 conversion is indeed dictated by thermal chemistry.

We would expect these trends to be the same for the CO_2 conversion, but it was not the case (Figure 3-8). Therefore, we will have to plot the species density profiles to understand the lower CO_2 conversion at condition γ (see section 3.3.5 below). Furthermore, we need to understand why the temperature profiles follow the above trends, with a rise as the O_2 fraction in the mixture increases and a drop as the CH_4 fraction rises. This, in turn, is directly linked to the enthalpy profiles, which we will discuss first.

Figure 3-11 illustrates the enthalpy profiles for all conditions, obtained by integrating the total heat capacity with respect to T .

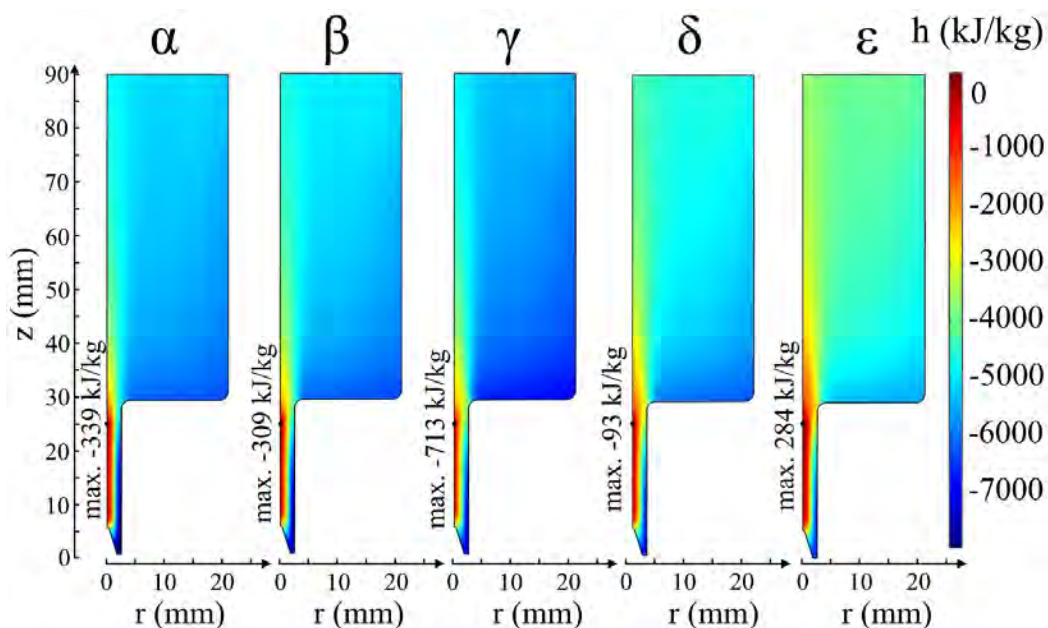


Figure 3-11 - Total enthalpy profiles for all conditions of Table 3-4.

First, the enthalpies at the inlet for low O_2 and rather low CH_4 conditions (α and β, i.e., -7978 kJ/kg and -7509 kJ/kg) are lower (i.e., more negative) than for the higher CH_4 and higher O_2 conditions (γ, δ, and ε, i.e., -7056 kJ/kg, -6809 kJ/kg and -6535 kJ/kg). This is expected, due to the small molar enthalpy of CO_2 at 293 K (-393.5 kJ/mol). The difference between the maximum enthalpy and the inlet enthalpy directly affects the maximum temperature; a smaller difference yields a higher maximum temperature. Thus, the lower (= more negative) maximum enthalpy of condition γ (-713 kJ/kg) with respect to conditions α (-339 kJ/kg) and β (-309 kJ/kg) explains the increase in temperature at condition γ (see Figure 3-10), despite a somewhat lower plasma power (cf. Table 3-4). Likewise, the less negative enthalpy in condition δ (from a maximum of -713 kJ/kg at condition γ, to a maximum of -93 kJ/kg) explains the lower temperature shown in Figure 3-10. This trend continues and is even more pronounced for condition ε (highest CH_4 and O_2 fractions and lowest CO_2 fraction), where the maximum enthalpy is positive (+284 kJ/kg) and the temperature is clearly lower (Figure 3-10).

The total enthalpy is temperature- and species-dependent. Therefore, to fully understand the change in enthalpy and, by extension, the change in temperature, we need a better understanding of the species composition in the plasma bulk and afterglow.

3.3.5 Plasma species analysis

Figure 3-12 depicts the molar fraction profiles of the dominant eight species (CO_2 , CH_4 , O_2 , CO , H_2O , H_2 , C_2H_2 , and HCHO) at conditions α , β , and γ .

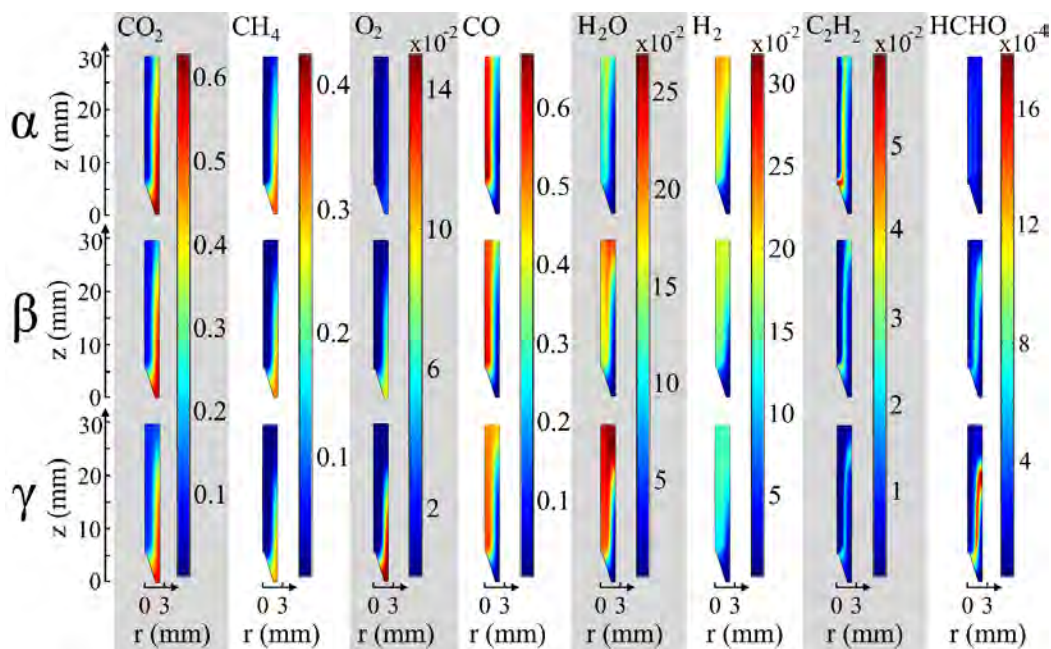


Figure 3-12 - Molar fraction profiles of CO_2 , CH_4 , O_2 , CO , H_2 , C_2H_2 , and HCHO , for conditions α , β , and γ .

The CO_2 and CH_4 plots show that these molecules are destroyed closer to the inlet already, at a higher O_2 fraction (i.e., condition β with respect to α , and condition γ with respect to β). This can be understood as a direct effect of the higher temperature plotted in Figure 3-10. It also explains the higher CH_4 conversion, as shown in Figure 3-8.

All the CH_4 is converted in the center of the plasma (see dark blue color in Figure 3-12), but not necessarily at the walls. This is one of the reasons why the overall measured conversion is not 100% (see Figure 3-8); note that the reason is not due to backreactions in the afterglow, as follows from the afterglow analysis (see section 3.3.7 below). The hotter the plasma, the higher the temperature near the walls/anode ring (see Figure 3-10), leading to greater conversion there as well. At condition α , not all CH_4 is converted at the walls (see Figure 3-12), while more is converted at condition β , and virtually all is converted at condition γ . Indeed, the molar flow rates of CH_4 at the end of the reactor for conditions α , β and γ are 3.87×10^{-5} mol/s, 7.23×10^{-6} mol/s and 7.63×10^{-7} mol/s, respectively.

In the high-temperature plasma core, the gas mixture mainly consists of the products CO, H₂, and H₂O, along with unreacted CO₂. The molar fractions of CO and H₂ both drop with increasing O₂ fraction, with CO reaching a maximum of 0.67 at condition α , and 0.54 at condition γ , and H₂ reaching 0.23 at condition α , and 0.19 at condition γ . The maximum H₂O molar fraction increases from 0.16 at condition α , to 0.27 at condition γ . This shift in gas composition explains the change in the total enthalpy of Figure 3-11. Indeed, the molar enthalpy of CO, H₂, and H₂O at 3000 K is -17.0 kJ/mol, 88.7 kJ/mol, and -114.2 kJ/mol, respectively. Therefore, we can understand that the higher O₂ fraction in the mixture (and thus lower CO₂ and CH₄ fractions) shifts the composition from a high molar fraction of CO and H₂ in the plasma to a higher fraction of H₂O, resulting in the lower (= more negative) enthalpy at condition γ , due to the low molar enthalpy of H₂O with respect to the molar enthalpies of CO and H₂. This more negative total enthalpy can explain the higher temperature and thus partly account for the higher CH₄ conversion under condition γ . To evaluate whether there is also a change in chemistry at high O₂ fractions, we present a chemical analysis on the production and destruction of C₂H₂ in Figure 3-14 below.

It is also clear from Figure 3-12 that the destruction of CH₄ at condition γ happens closer to the inlet, compared to the destruction of CO₂. Indeed, CH₄ and O₂ react at lower temperatures, allowing the production of polyatomic radicals and stable species, of which C₂H₂ and HCHO are examples plotted. In the case of C₂H₂, it is clear that the higher temperature destroys this product due to reaction with oxygenated species. Indeed, the maximum C₂H₂ molar fraction under condition γ is 0.024, whereas under condition α it reaches 0.056. At condition γ , almost all C₂H₂ is destroyed after the plasma, reducing its molar fraction to 8.2×10^{-6} , while the molar fraction at condition α drops only to 0.027 after the plasma, indicating that either C₂H₂ is destroyed due to higher temperatures at condition γ , or upon reaction with oxygenated species, like HCHO.

On the other hand, the molar fraction of HCHO increases from 4×10^{-4} at condition α , to 0.0018 at condition γ . This species is, however, short-lived and immediately destroyed again when reaching any higher temperature. Many products of the reaction of CH₄ and O₂, as mentioned above, behave in the same way as HCHO, having only very short lifetimes (e.g., CH₃O, CH₂CO, HCCO, C₂H₅, etc.). To determine whether a higher HCHO molar fraction or a higher temperature at higher O₂ content reduces the selectivity of C₂H₂, we need to look at conditions δ and ϵ , which have lower temperatures but equal O₂ fractions.

Figure 3-13 depicts the molar fraction profiles of the same eight species (CO_2 , CH_4 , O_2 , CO , H_2O , H_2 , C_2H_2 , and HCHO) at conditions γ , δ , and ϵ , which allows us to compare the effect of a higher CH_4 fraction (and thus a lower CO_2 fraction) at a constant O_2 fraction.

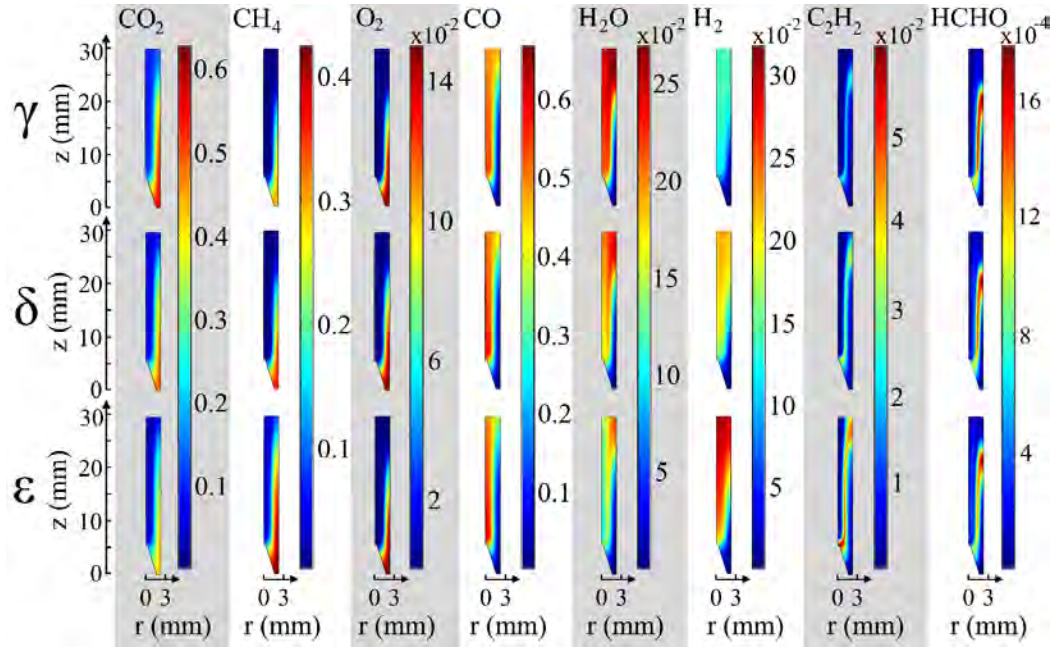


Figure 3-13 - Molar fraction profiles of CO_2 , CH_4 , O_2 , CO , H_2 , C_2H_2 , and HCHO , for conditions γ , δ , and ϵ .

As shown in Figure 3-13, adding CH_4 to the mixture (i.e., from γ to δ to ϵ) results in the reverse trends shown from Figure 3-12. The higher CO and, especially, H_2 molar fractions in the plasma center lead to a higher enthalpy, which explains the drop in temperature in Figure 3-10. Furthermore, more CH_4 in the mixture results in a higher molar fraction of C_2H_2 , reaching a maximum of 0.06 under condition ϵ . However, the molar flow rate at the end of the reactor at condition ϵ is 2.35×10^{-5} mol/s, i.e., very similar to the value at condition α , i.e., 2.22×10^{-5} mol/s.

As the maximum temperatures are 3019 K for condition ϵ and 2981 K for condition α , the C_2H_2 selectivity largely depends on temperature. To better understand the effect of transient species on plasma behavior, such as C_2H_2 , which are not the main reaction products but are produced in the plasma, destroyed, and still constitute a significant portion of the molar composition inside the plasma, we analyzed the production and destruction of C_2H_2 . Specifically, we conducted a comprehensive analysis of the effect of C_2H_2 on the heat balance.

In Figure 3-14, the rates of the most important production and destruction reactions of C_2H_2 are plotted for condition α (a) and γ (b), as a function of radial position, at $z = 14$ mm.

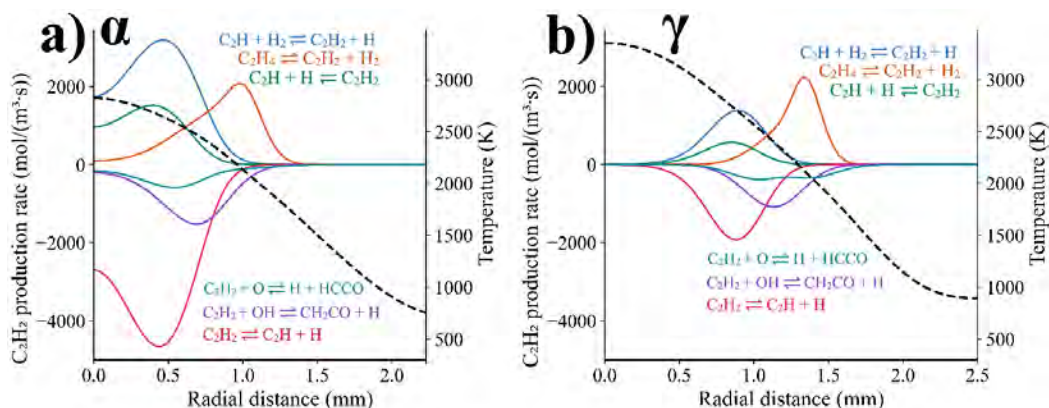


Figure 3-14 - Rates of the most important C_2H_2 production and destruction reactions, as a function of the radial distance at $z = 14$ mm, for condition α (a) and γ (b). The black dashed line represents the temperature profile (on the right y-axis).

Figure 3-14(a) indicates three important formation reactions: at higher radial distances (around $r = 1$ mm), C_2H_2 is mostly formed from C_2H_4 , while closer to the center of the plasma, at higher temperatures, C_2H_2 is mainly formed from C_2H . Furthermore, there is no significant C_2H_2 formation from any oxygenated species. The destruction of C_2H_2 is mostly to C_2H . The reactions of C_2H_2 with O or OH are less important.

Figure 3-14(b) illustrates that the most important production and destruction reactions have not changed from condition α , but the rates have shifted. The production rates of C_2H , as well as the destruction rate towards C_2H , are lower, increasing the relative importance of the other pathways. The production of C_2H_2 from C_2H_4 ($C_2H_4 \rightleftharpoons C_2H_2 + H_2$) is now the most important production process, although its maximum reaction rate remains more or less the same as in condition α . The maximum destruction rate of C_2H_2 to C_2H and H ($C_2H_2 \rightleftharpoons C_2H + H$), which does not involve any oxygenated species, is reduced from $-4660 \text{ mol}/(m^3 \cdot s)$ in condition α to $-1930 \text{ mol}/(m^3 \cdot s)$ in condition γ . These changes result in lower production and destruction rates of C_2H_2 under condition γ , demonstrating the importance of the temperature profile and, thus, indicating that the change in Figure 3-12 for the C_2H_2 molar fraction is not due to new chemical pathways.

These changes in reaction rates affect the heat balance in the system. Therefore, the heat produced and lost by chemical reactions should be analyzed for conditions α and γ (see next section).

3.3.6 Heat balance analysis

Figure 3-15 depicts the heat released (or absorbed) by the various reactions for condition α (a) and γ (b) at $z = 14$ mm. As these are net rates, the species in bold in each reaction are produced by the net reaction rate. Furthermore, the reactions are written as endothermic; positive values, corresponding to a release of heat, indicate the formation of species at the left side of the reaction, while negative values, indicating a removal of heat, represent the formation of species at the right side of the reaction. Only the most important reactions contributing to heat absorption or release are plotted. Therefore, the black line, which represents the total heat absorbed by all reactions, does not exactly match the sum of the separate reaction heats in this figure. Not all reactions could be listed in the plot, for clarity; they are indicated with labels (a-f): (a) $\text{C}_2\text{H}_2 + \text{H} \rightleftharpoons \text{C}_2\text{H} + \text{H}_2$, (b) $\text{CH}_2\text{CO} + \text{H} \rightleftharpoons \text{CH}_3 + \text{CO}$, (c) $\text{H} + \text{HCHO} \rightleftharpoons \text{CH}_3 + \text{O}$, (d) $\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH}$, (e) $\text{CO} + \text{H}_2 \rightleftharpoons \text{H} + \text{HCO}$, (f) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{HCO} + \text{OH}$.

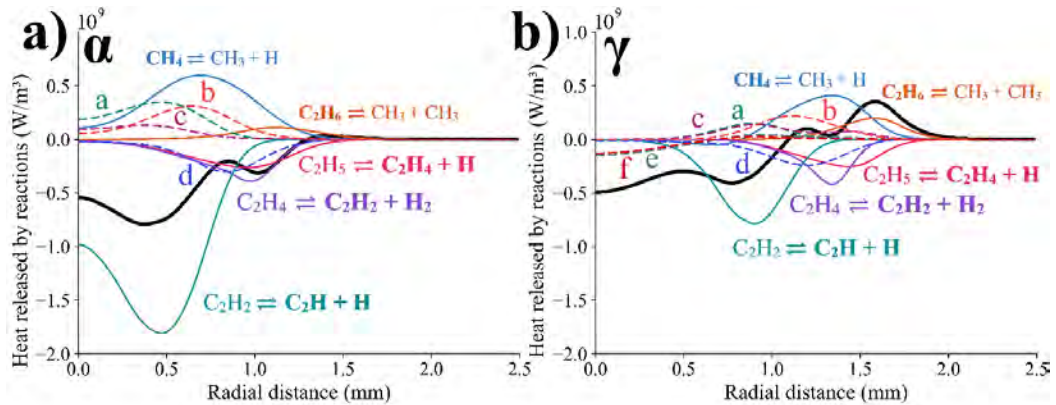


Figure 3-15 - Heat released (or absorbed, when negative) by the most important reactions, and for the sum of all reactions (black), as a function of the radial distance at $z = 14$ mm, for condition α (a) and γ (b). Reactions a-f are: (a) $\text{C}_2\text{H}_2 + \text{H} \rightleftharpoons \text{C}_2\text{H} + \text{H}_2$, (b) $\text{CH}_2\text{CO} + \text{H} \rightleftharpoons \text{CH}_3 + \text{CO}$, (c) $\text{H} + \text{HCHO} \rightleftharpoons \text{CH}_3 + \text{O}$, (d) $\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH}$, (e) $\text{CO} + \text{H}_2 \rightleftharpoons \text{H} + \text{HCO}$, (f) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{HCO} + \text{OH}$.

Figure 3-15(a) indicates that for condition α , the most important reaction removing heat via chemistry is the dissociation of C_2H_2 to C_2H and H , with a maximum heat removal of $1.8 \times 10^9 \text{ W/m}^3$. This indicates the importance of the C_2H_x chemistry on the plasma heat balance.

Figure 3-15(b) illustrates the heat released in condition γ . The temperature profile under these conditions was plotted in Figure 3-14(b) and should be kept in mind when discussing the major differences. Firstly, the trend shown in Figure 3-14 has significant implications here as well: the lower production and destruction rates of C_2H_2 compared to condition α affect not only the molar fraction of C_2H_2 but also heat exchange. The maximum heat absorbed by the reaction of C_2H_2 into C_2H and H drops to $8 \times 10^8 \text{ W/m}^3$, and this reduces the amount of heat removed at $r = 0.8 \text{ mm}$. Moreover, there is even a release of heat upon chemical reactions at $r = 1.6 \text{ mm}$ (cf. black curve), driven by the same reactions releasing heat in Figure 3-15(a). The reduced heat removal via reactions at condition γ allows for a higher temperature to be reached, which is accompanied by several new endothermic reactions (e and f in Figure 3-15(b)). As the total heat balance must be satisfied at each position, the absorbed and released heat at each position must be compensated by the other heat balance terms, as we will explain below.

In Figure 3-16, we plot the important terms of the heat balance equation as a function of radial distance, at $z = 14 \text{ mm}$, for conditions α (a) and γ (b). The terms for enthalpy diffusion, axial conduction, and both radial and axial turbulent conduction are omitted due to their low importance. All the heat balance equation terms are moved to the right side, resulting in a zero sum.

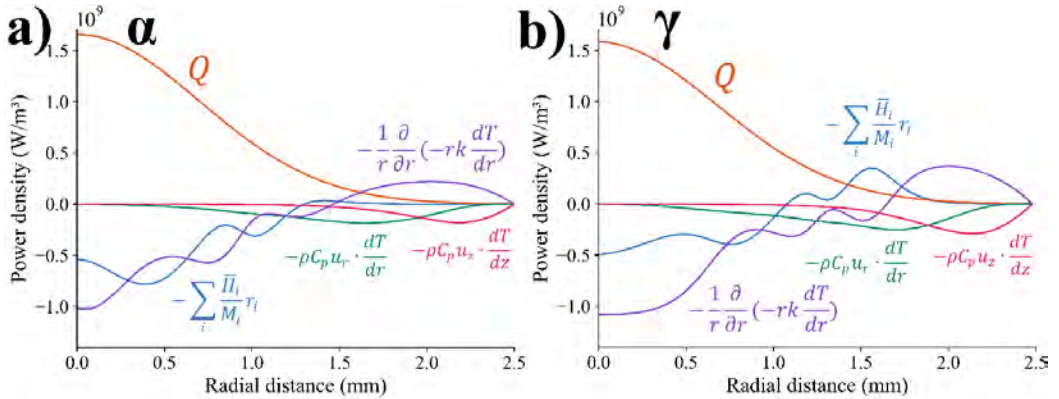


Figure 3-16 - Most important terms in the heat balance equation, as a function of the radial distance at $z = 14 \text{ mm}$, for condition α (a) and γ (b).

Figure 3-16(a) clearly indicates the importance of the terms due to radial conduction (purple) and the heat of reactions (blue) near the center, where the convective heat losses (green and red) are near zero. Note that the heat of reaction term is equal to the (inverted) black line in Figure 3-15(a), which shows the origin of the features in this term.

The radial component of the conductive heat loss compensates for these features, keeping the sum of these two terms equal to the heat source Q (orange). As Figure 3-14(a) shows no such features in the radial temperature profile at $z = 14$ mm, these features in the radial thermal conductivity term originate from the thermal conductivity k . Essentially, this means that k cannot be considered constant in any global model describing this chemistry and must include the effects of chemical reactions to satisfy a correct heat balance profile. Importantly, this stresses the limitations of commonly used global/OD models. Furthermore, near the edges, the radial conduction compensates for the heat losses from both radial and axial convective terms, which again, due to the complexity of the flow field, cannot be considered in a flow-averaged global model.

Figure 3-16(b) illustrates the same trends, with a major difference being the effect of k at $r = 1.6$ mm, where exothermic reactions force k to displace heat, while for condition α , at $r = 1.6$ mm, k deposits heat. This demonstrates once again the significant effect of reaction heat on thermal conductivity.

To summarize, the heat balance equation shows that the significant features in the thermal conductivity plot depend on the reaction heat exchange and the user-defined heat source; these, in turn, influence the temperature profile, determine the gas composition, and consequently also the reaction heat exchange. This is an important finding of our model, because it reveals that the thermal conductivity cannot be approximated via linear or quadratic dependencies on the gas temperature. The non-locality of the system, see also section 3.3.8 below, influences the thermal conductivity, as it is coupled to the gas composition. Hence, it stresses the need to use a fully coupled 2D axisymmetric model.

3.3.7 Afterglow analysis

As the measured conversion and product compositions do not necessarily correspond to the situation right after the plasma reactor, but can be subject to additional chemistry in the plasma afterglow, we can also use our model to obtain more insights into the molar fractions and temperature in the afterglow. Figure 3-17 shows the temperature and molar fractions of species (> 0.01) in the afterglow, starting after the heat source ($z = 30$ mm) until the outlet ($z = 89$ mm), at $r = 0$ mm. The solid and dashed lines represent conditions α and γ , hence an O_2 fraction in the mixture of 3 and 15%, respectively.

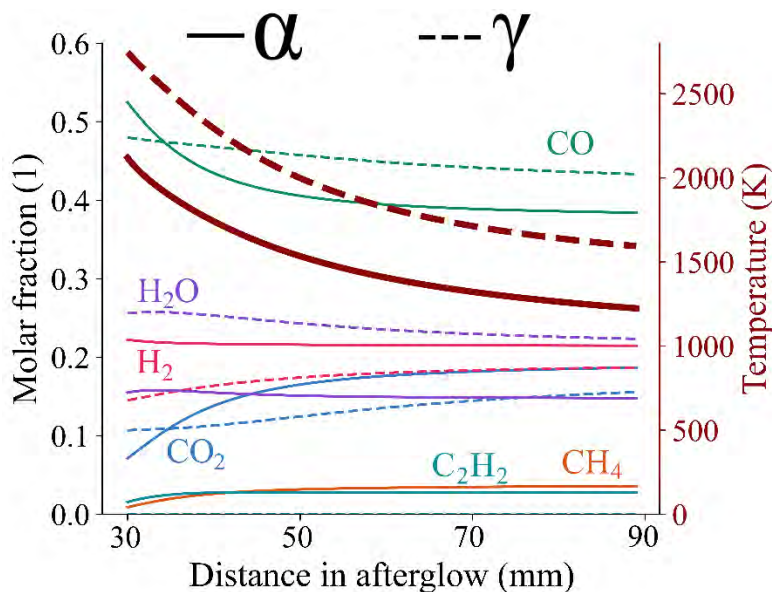


Figure 3-17 - Temperature and molar fractions of CO_2 , CH_4 , O_2 , CO , H_2 , C_2H_2 , and H_2O , plotted over the afterglow ($z = 30 \text{ mm}$ to $z = 89 \text{ mm}$, for $r = 0 \text{ mm}$), for conditions α and γ . 30 mm denotes the beginning of the afterglow.

First, the trends described earlier are again visible at the beginning of the afterglow. Adding more O_2 (i.e., from condition α to γ) results in an increase in H_2O , the removal of C_2H_2 and CH_4 , and a drop in H_2 molar fraction. Although the CO_2 molar fraction rises as a function of distance in the afterglow at condition α , this is not due to the recombination of CO into CO_2 . Indeed, due to the presence of H atoms, there is no O_2 present in the afterglow, as the O atoms rather react with H atoms into H_2O instead of forming O_2 . Therefore, the formation of CO_2 would proceed via the water-gas shift reaction, in which CO and H_2O react to form H_2 and CO_2 . As neither the H_2 nor the H_2O molar fraction significantly changes upon rising distance in the afterglow, we can conclude that the water-gas shift reaction does not occur. Furthermore, for the water-gas shift reaction to occur at this timescale (i.e., a few milliseconds), the gas should be above 2000 K, which is not the case at condition α . The change in the molar fraction of CO_2 with increasing distance should thus have another cause. Indeed, looking at Figure 3-12 (for condition α), we can see that the CO_2 molar fraction at the top clearly varies in the radial direction. This is due to the low CO_2 conversion near the walls (similar to the CH_4 conversion trend discussed earlier).

In conclusion, our model reveals that the increase in CO_2 and decrease in CO molar fraction with distance in the afterglow (Figure 3-17) are not due to chemistry but simply to the mixing of gas molecules near the walls and at the center. The same is true for the increase in CH_4 and C_2H_2 molar fractions in the afterglow at condition α . Species with a molar fraction that is less radially dependent, e.g., H_2 (see Figure 3-12), do not exhibit a large variation in molar fraction as a function of distance in the afterglow, which demonstrates that there are no significant chemical reactions occurring in the afterglow, as the temperature is too low already.

In contrast to this, the afterglow at condition γ shows some variation in H_2 and H_2O molar fractions, as well as in the CO and CO_2 fractions. Figure 3-12 and Figure 3-13 demonstrate that this is not due to mixing, as the molar fraction of H_2 is not radius-dependent at the end of the plasma. Instead, the higher H_2O fraction and lower H_2 fraction at condition γ allow the exothermic water-gas shift reaction to occur in the model. This reaction enhances the H_2 molar fraction from 0.145 to 0.187, and the CO_2 molar fraction from 0.107 to 0.156. Hence, this explains the drop in CO_2 conversion in Figure 3-8 for condition γ . As Figure 3-8 does not show the same drop in the experimental CO_2 conversion, we may conclude that the afterglow is probably too hot in the model, which gives rise to chemical reaction pathways (such as the water-gas shift reaction) that are not occurring in reality, creating the discrepancy between calculated and measured CO_2 conversion trend towards condition γ .

Figure 3-18 illustrates the temperature and molar fractions of species (> 0.01) in the afterglow, starting after the heat source ($z = 30$ mm) until the outlet ($z = 89$ mm), with the solid and dashed lines represent condition γ and ϵ , hence a low CH_4 and high CO_2 fraction, and a high CH_4 and low CO_2 fraction, respectively, at constant O_2 fraction of 15%.

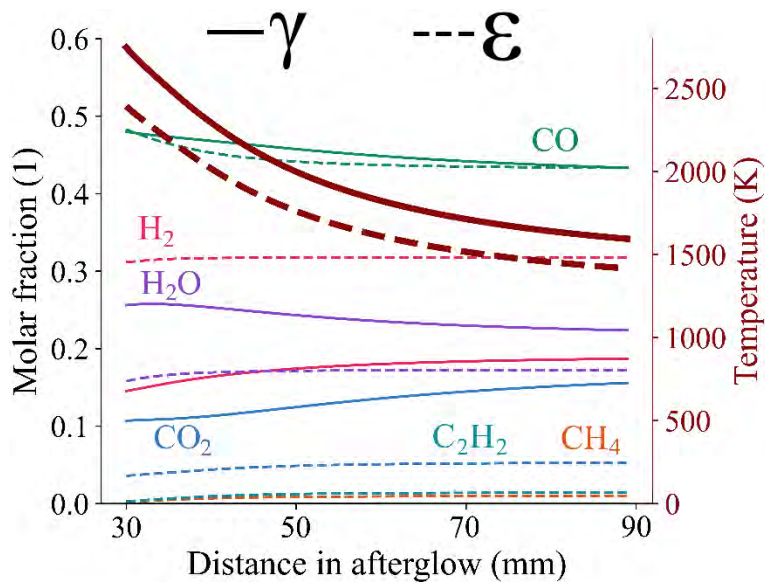


Figure 3-18 - Temperature and molar fractions of CO_2 , CH_4 , O_2 , CO , H_2 , C_2H_2 , and H_2O , plotted over the afterglow ($z = 30$ mm to $z = 89$ mm, for $r = 0$ mm), for condition γ and ϵ . 30 mm denotes the beginning of the afterglow.

A higher CH_4 fraction in the mixture (condition ϵ) results in a lower H_2O and a higher H_2 molar fraction in the plasma (see Figure 3-13). Combined with the lower temperature (see Figure 3-10), the water-gas shift reaction does not proceed in the model, in contrast to condition γ . Worth noting is the drop in molar fraction of CO_2 , reaching 0.052 at the outlet for condition ϵ , while it is 0.156 for condition γ and 0.187 for condition α (cf. Figure 3-17). Indeed, at condition γ , the CO_2 molar fraction rises from 0.107 to 0.156 (from $z = 30$ mm to $z = 89$ mm), which is much more than the rise in CO_2 molar fraction at condition ϵ (from 0.036 to 0.053). Together with the H_2O and H_2 trends (i.e., their molar fractions barely change upon rising distance for condition ϵ), this indicates again that the water-gas shift reaction does not occur in the afterglow at condition ϵ . The small increase in C_2H_2 and CH_4 fraction at condition ϵ is again due to mixing of the molecules from the center and the walls, as discussed before.

3.3.8 Importance of diffusive and convective fluxes

Finally, we want to stress the importance of diffusion and convective fluxes in determining the gas composition and temperature, and in general, the reactor performance. In Chapter 1, we mentioned that previously, LCE approaches were used in multidimensional CFD plasma models [73,74,105–107]. The validity of these models

depends on the local character of the chemistry, i.e., whether temperature fully determines the chemical composition. To assess whether this assumption is valid at the conditions under study, we performed additional simulations with no convective fluxes and a small diffusion coefficient of $1 \times 10^{-4} \text{ m}^2/\text{s}$, using temperature profiles equal to those in the coupled model. Figure 3-19 compares our model, including both fluxes (full model; F), with a model neglecting the convective flux and very limited diffusion (so-called local model; L) for the CO_2 , H_2 , CO , and H molar fractions, at condition γ .

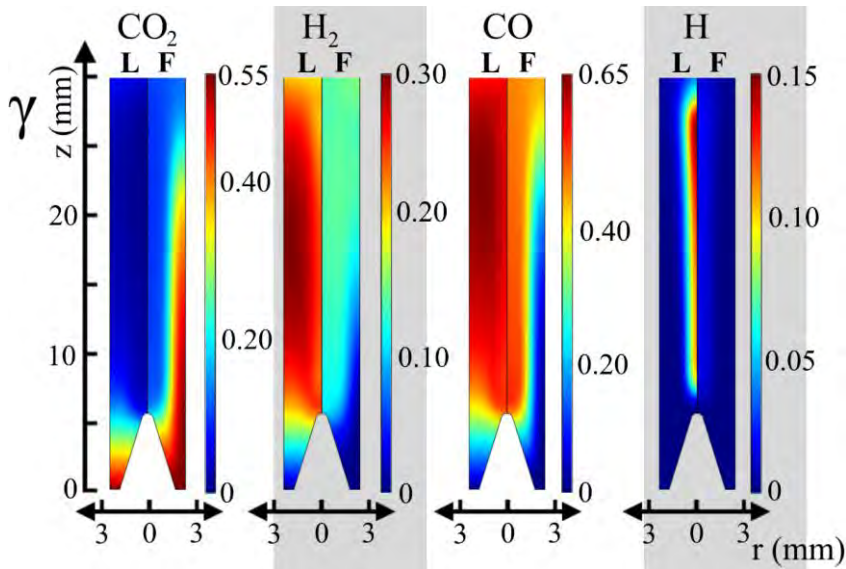


Figure 3-19 - Molar fractions of CO_2 , H_2 , CO , and H , obtained from a local, low flux (L) model and a full model including diffusive and convective fluxes (F), at condition γ .

There is a clear difference in the results between the local and full models, including the computed fluxes. This shows that the LCE approach, as used in previous models in the literature, is not applicable to the conditions under study here, i.e., OCRM in a warm plasma, at the timescale over which the gas typically passes through the APGD (1 to 3 ms). The chemistry is too slow to reach equilibrium, even in the center of the plasma; cf. the molar fraction of H , which reaches 0.15 in the local model, while it is negligible in the full model.

As the flow is predominantly described by the axial direction (see Figure 3-7), radial concentration gradients in the local model (L), which are absent in the full model (F), are due mostly to diffusive fluxes and not convective fluxes. This further stresses the importance of including both correct diffusive and convective fluxes in this model.

To summarize, multidimensional models using the LCE approach can differ significantly from models that include the correct fluxes, as demonstrated here for OCRM in warm plasma. Indeed, the temperature and chemical composition profiles strongly depend on these fluxes; therefore, the only correct way to describe this system is with a fully coupled model. Therefore, more generally, the LCE approximation should be used with caution in all chemistries within warm plasma models. Applying the LCE approximation in this case would overestimate the conversion, and, for endothermic reactions, a model that includes heat transfer calculations using the LCE approximation would severely underestimate the true plasma temperature.

3.3.9 Reaction pathway analysis

The aforementioned temperature changes will affect the conversion, as more CO_2 and CH_4 will be converted when a larger portion of the reactor reaches a sufficient temperature. However, the effect of O_2 on the DRM chemistry should not be neglected; therefore, we performed a reaction analysis under a condition without O_2 and under condition γ out of curiosity. Figure 3-20 shows the multidimensional reaction pathway analysis for the condition 65/35/0 $\text{CO}_2/\text{CH}_4/\text{O}_2$, indicating where most of the shown species are present in the plasma, as well as the temperature profile of the plasma. Species plots in Figure 3-20 do not indicate how much of a species is present in a reactor, but rather where most of it resides, with light yellow indicating greater presence and black indicating absence. Note that such a multidimensional reaction pathway analysis, showing not only the reaction pathways but also where in the plasma these reactions are dominant (which appears different for different reactions), is not possible with a global (0D) model, mostly used in literature for reaction pathway analysis [68,137,143], but really requires a more-dimensional model, as used in our work.

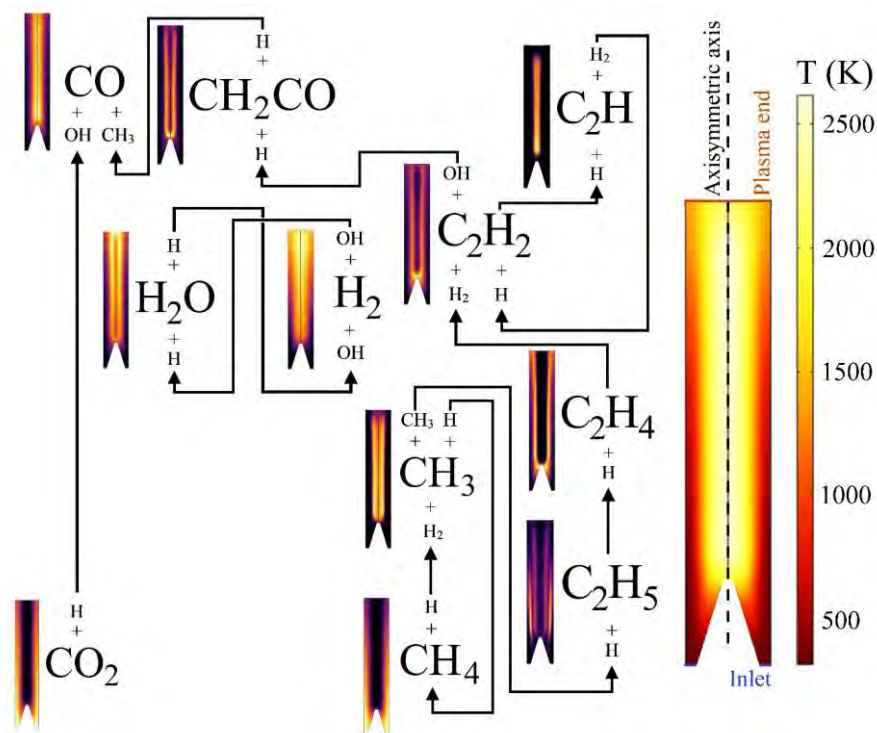


Figure 3-20 - Multidimensional reaction pathway analysis for condition 65/35/0 CO₂/CH₄/O₂, indicating where most of the shown species are present in the plasma (left), with the temperature profile of the plasma shown at the right.

Only the species with the highest concentrations are plotted to show a clear chemical pathway. Starting the pathway analysis from the bottom-left corner, we find that almost all CO₂ conversion proceeds via the reaction of CO₂ with H to form CO and OH. The latter is an important radical in many pathways, i.e., the shift between H₂ and H₂O (as indicated in the middle of the figure). The reaction of OH with H₂ to form H and H₂O is shown in both directions, because they are important in different regions, as indicated by the 2D species concentration profiles. The formation of H₂O from H₂ is important near the edges of the plasma, where H₂ is formed from the reaction of CH₄ and H, producing CH₃ and H₂, but it also stems from the reaction of C₂H₄ to C₂H₂ and H₂ (as also indicated in the middle-bottom part of the figure). H₂ is then again formed from H₂O in the center of the plasma. Note that the plot of H₂O shows a smaller fraction of H₂O present in the center due to this reaction. Furthermore, the production of C₂H₂ from CH₄ passes through multiple hydrocarbons. Indeed, C₂H₅ is formed from CH₃, which then generates C₂H₄

closer to the center of the plasma, and eventually C_2H_2 even closer to the center (see the right-hand side of the figure). We can see that additional CO is formed from reactions of C_2H_2 with, again, OH, leading to the formation of CH_2CO , which eventually decomposes with H to CH_3 and CO (left top of the figure).

Figure 3-21 illustrates the multidimensional reaction pathway analysis for condition γ , indicating where most of the depicted species are present in the plasma and showing the plasma temperature profile.

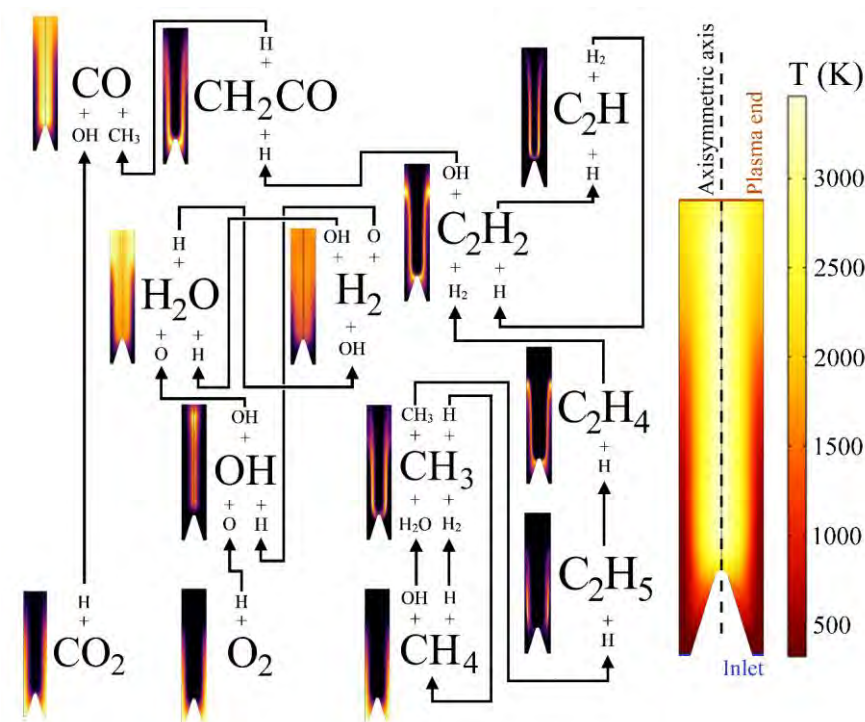


Figure 3-21 - Multidimensional reaction pathway analysis for condition γ , indicating where most of the shown species are present in the plasma (left), with the temperature profile of the plasma shown at the right.

The most pronounced difference in the chemistry relative to Figure 3-20 is the presence of O radicals from O_2 , which enables more reactions involving H_2 and H_2O . The reaction of H_2 with O is an additional source for OH radicals, which can react with themselves to form H_2O and O. These additional OH radicals allow for an additional reaction to destroy

CH_4 , as the latter now also reacts with OH radicals to form CH_3 and H_2O . The presence of C_xH_y species is now much farther from the plasma center compared to Figure 3-20. This is attributed to the higher temperature, forcing stronger temperature gradients.

These strong gradients result in a smaller space available to species that will react away at higher temperatures. This is also why much less C_2H_2 is found near the model outlet in the 15 % O_2 case, which is consistent with the experiments. Furthermore, as mentioned in the introduction, the Kassel mechanism [144] describes the formation of solid carbon from C_2H_2 and C_2H , both of which are more present in and near the edges of the plasma in Figure 3-20. Even though solid carbon particles are not directly accounted for in our model, the increased presence of its precursor, according to the Kassel mechanism, also indicates greater solid carbon formation in condition 65/35/0 than in condition γ , as observed in our experiments.

Furthermore, Figure 3-21 shows that the formation of H_2O from O_2 is mainly via the reaction of two OH radicals. This means that a rise in OH radical density, which linearly increases the removal rate of solid carbon ($\sim[\text{OH}]$), results in a quadratic increase of the production rate of H_2O ($\sim[\text{OH}]^2$). Hence, the effect of H_2O production is larger than the effect on solid carbon removal.

Finally, we also understand that C_2H_2 , and thus solid carbon, will be removed by an increase of OH radicals in the plasma, as the pathway analysis shows the production of CH_2CO in this case. Although our pathway analysis indicates that OH radicals are formed via O_2 addition, we could also consider an alternative source of OH radicals, e.g., H_2O . Hence, the combined conversion of CO_2 and CH_4 with H_2O addition, i.e., so-called bi-reforming of methane, might also be interesting to investigate in future work, by someone else.

3.4 Conclusion

We developed a new, fully coupled multidimensional model for plasma-based gas conversion, based on a 2D axisymmetric model (describing the gas flow, heat balance, and species transport and chemistry), in combination with a 3D gas flow model and a 0D detailed plasma chemistry model (which both provide input to the 2D model). The combination of these models helps to understand the chemistry and physics occurring in warm plasmas.

We applied this model to an atmospheric pressure glow discharge plasma in a CO_2/CH_4 mixture with O_2 addition (so-called oxidative CO_2 reforming of CH_4 ; OCRM) and

compared the calculated CO₂ and CH₄ conversion and product composition with experiments performed at exactly the same conditions. Specifically, we compared our results across five conditions, each reflecting a different inlet gas composition. Although the absolute values still show some discrepancies (illustrating the complex physical and chemical system, which cannot all be captured yet by our model), we found a reasonable agreement in the trends for the different conditions, certainly keeping in mind that our model did not use any fitting to reach agreement with the experiments. Therefore, the model can be used to explain the observed experimental trends.

Our model predicts the highest gas temperature for the highest O₂ fraction in the mixture (condition γ, as compared to conditions α and β), and the temperature drops upon higher CH₄ fractions (conditions δ and ε). This can be explained by the higher amount of H₂O present in the plasma at the highest O₂ fraction, which has a lower molar enthalpy than CO and H₂, leading to a lower (more negative) overall enthalpy for condition γ and the highest temperature. This higher gas temperature can explain the increased CH₄ conversion with increasing O₂ fraction in the mixture, as also observed experimentally. In addition, chemical reactions also allow for a lower enthalpy of the resulting gas mixture in the plasma, showing the thermal character of the conversion process.

The calculated CO₂ conversion reaches its minimum at the highest O₂ fraction and the lowest CH₄ fraction in the mixture (condition γ), whereas the measured CO₂ conversion does not show clear variation across the conditions tested. The calculated trend arises because our model predicts the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) in the afterglow, due to the higher H₂O molar fraction at the highest O₂ and lowest CH₄ fractions in the mixture (also observed experimentally). However, the fact that the measured CO₂ conversion does not exhibit the same trend indicates that the afterglow reaction is overestimated in the model, likely due to too slow cooling. Therefore, in future work, we will study how our model can lead to faster cooling in the afterglow (likely due to increased gas turbulence), to better reflect reality.

We also demonstrate that approximations of previous models, i.e., both for global models, which assume a constant or temperature-dependent thermal conductivity, as well as for multidimensional models, using a local chemical equilibrium approach, would not be valid at the conditions under study, as these approximations do not reflect the true complexity of the system, hence, stressing the need for a fully coupled 2D axisymmetric model.

In general, our new model can capture the major physics and chemistry, even in complex gas mixtures, such as $\text{CO}_2/\text{CH}_4/\text{O}_2$, solely using the plasma power, gas flow rate, gas inlet composition, and reactor geometry as input, while all other quantities are self-consistently calculated and no fitting is used. This indicates an important step towards predictive modeling for plasma-based gas conversion. We will present an even further improved version of this model in Chapter 5 below.

Chapter 4

Performance insights into plasma-based NH_3 cracking from a global model

The content of this chapter is in part based on:

Plasma-based NH_3 Cracking: A Better Insight in the Performance by Chemical Kinetics Modeling

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This chapter examines performance characteristics of (warm-)plasma-based NH₃ cracking using a detailed plasma chemical kinetics model across a wide range of gas temperatures ($T_g = 1000\text{--}6000\text{ K}$) and electron temperatures ($T_e = 0\text{--}3.5\text{ eV}$, i.e., $0\text{--}40,000\text{ K}$). NH₃ conversion increases with both temperatures, but the T_g -dependence flattens near full conversion. Pure thermal cracking reaches full conversion at 2300 K and 10 ms , while plasma achieves full conversion at $T_e > 2.75\text{ eV}$ for all T_g , even the lowest T_g values investigated. At $T_g < 2700\text{ K}$, high T_e dramatically reduces the time for full conversion, for example, from thousands of years (thermal) to milliseconds (plasma) at $T_g = 1100\text{ K}$, while differences vanish at $T_g > 2700\text{ K}$. Product composition follows thermal equilibrium, showing negligible T_e influence. Importantly, we also suggest strategies for performance improvement. The best EC for typical warm plasmas with continuous power is predicted to be $197\text{ kJ.mol}^{-1}\text{-NH}_3$ at 2500 K , where thermal pathways dominate. Reducing vibrational energy losses suggests potential improvement at $T_g \approx 1500\text{ K}$, predicting an EC of $157\text{ kJ.mol}^{-1}\text{-NH}_3$, for so-called “plasma-initialized” thermal cracking. Further reduction in EC should be feasible via heat recovery. Overall, our model shows that plasma cracking offers rapid NH₃ conversion with reasonable EC.

4.1 Introduction

As discussed in Chapter 1, NH_3 is a great H_2 carrier to support a growing H_2 economy. Converting H_2 into NH_3 benefits from existing infrastructure for large-scale storage and long-distance transport [145]. Unlike liquefied H_2 , NH_3 does not require cryogenic temperatures (20 K) [146], reducing both energy demand and leakage risks. Moreover, partial NH_3 cracking improves its combustion characteristics: while pure NH_3 burns slowly due to its limited chemical reactivity, an $\text{NH}_3\text{--H}_2$ mixture exhibits enhanced ignition and flame speed, comparable to those of hydrocarbon fuels [147]. This concept supports applications ranging from on-board cracking for transportation to stationary power systems. To make the $\text{NH}_3\text{--H}_2$ cycle practical, however, improvements in overall energy efficiency and cost remain essential.

While the thermodynamic equilibrium shifts from NH_3 to N_2 and H_2 above 800 K, significant thermal NH_3 cracking generally occurs only near 1300 K [148], requiring hundreds of hours due to slow kinetics. Thermo-catalytic NH_3 decomposition can lower this temperature range to $\sim 600\text{--}1100$ K [45,149,150], yet large-scale implementation remains difficult. Ru-based catalysts exhibit the highest activity but are hindered by high cost (~ 3000 USD kg^{-1}), scarcity, and high environmental footprint (~ 2000 kg CO_2 kg^{-1} -Ru) [149]. Ni- and Fe-based alternatives are cheaper but require elevated temperatures (≥ 1100 K) for full conversion [150]. Consequently, fossil fuel combustion is still commonly employed, reintroducing CO_2 emissions [151]. While direct NH_3/H_2 combustion is under study, NO_x emissions remain problematic. Electrically heated reactors could offer cleaner operation but are limited by design and material constraints, warranting further investigation [45].

Recently, warm plasmas have gained interest in NH_3 cracking. As stated in Chapter 1, warm plasmas are a subtype of non-thermal plasmas, with the electron temperature (significantly) higher than the gas temperature (cf. $\sim 10,000$ s K of $T_e \gg T_g$). Still, T_g is clearly above room temperature, i.e., in the range of several thousand K [152]. These higher gas temperatures generally improve the efficiency of chemical processes, as widely demonstrated for CO_2 conversion [17,153] and CH_4 reforming [48,154,155]. In the case of NH_3 cracking, warm plasmas also exhibit promising results. For example, the EC in a non-thermal (warm) arc plasma torch (without and with catalyst) was reported to be 196 and 157 $\text{kJ}\cdot\text{mol}^{-1}\text{-NH}_3$, respectively [156], which is around five-fold less than the best results in a DBD reactor [157]. Recently, Fedirchuk et al. compared the performance of four different types of warm plasmas and again confirmed the promise of their EC

(around 200 kJ.mol⁻¹-NH₃, and even down to 146 kJ.mol⁻¹-NH₃) and conversion (around 50-60% and higher), becoming closer to practical targets of < 100 kJ.mol⁻¹-NH₃ [45,152].

Although warm plasmas have demonstrated encouraging results, the lack of fundamental knowledge about their intricate plasma dynamics limits further improvement. This gap underscores the importance of investigating plasma chemical kinetics to refine operational strategies.

In this regard, we conduct here a comprehensive plasma kinetics study on warm plasma NH₃ cracking, examining the effects of representative operating conditions: electron temperature (T_e), gas temperature (T_g), as well as residence time (t_{res}), using a detailed chemistry model. Our primary objective is to assess how the performance characteristics of warm plasma NH₃ cracking—specifically NH₃ conversion and corresponding EC, product composition, and the time required to reach full conversion—are influenced by the operating conditions, linking the investigated variations to the underlying chemical mechanisms. Based on our modeling insights, we ultimately attempt to explore optimization strategies for reducing the EC, thus improving overall process efficiency. To our knowledge, this is the first systematic kinetic investigation of warm plasma NH₃ cracking. Accordingly, it provides new and valuable insights into the roles of electron-impact and thermal chemistry in plasma NH₃ cracking across a wide range of conditions, and how they affect NH₃ conversion, EC, product composition, and the time required to reach full conversion. Last but not least, we offer guidance toward addressing current experimental challenges, particularly those related to energy efficiency.

4.2 Computational details

To study the plasma chemical kinetics of NH₃ cracking in warm plasma, we developed a 0D (global) model using the plasma module framework in COMSOL Multiphysics [108,123]. In a global model, spatial derivatives in the continuity equations are neglected, making the plasma spatially homogeneous, and the equations are only solved as a function of time. All the equations used in the global model were detailed in Chapter 2. When electron temperature (T_e) and gas temperature (T_g) are described as “fixed”, this means that energy is added or subtracted from the electron energy balance or the heavy species balance, respectively, to fix the temperatures.

4.2.1 Operating conditions of warm plasmas

There exist various types of warm plasmas, used for diverse gas conversion applications, such as gliding arc (GA) plasma [152–154,158], microwave (MW) plasma [57,159–161],

atmospheric pressure glow discharge (APGD) [135,152,162], and non-thermal arc plasma (NTAP) [152,156,163–167], each with different operating conditions, even depending on the configuration. For example, at atmospheric pressure, GA plasmas are characterized by T_e of 1.4–4 eV (corresponding to ca. 15,000–45,000 K) and T_g of 1000–3000 K [158]. MW plasmas typically have lower T_e values of 0.4–1.4 eV, but higher T_g , ranging from 2000 to 6000 K [159,168,169]. APGD plasmas operate at T_e of 0.6–2 eV and T_g of 1000–2500 K [135,162]. Finally, NTAPs, which typically operate at lower current than thermal arc plasmas (i.e., ~few A [156,166] vs ~100s of A [163,165]), can reach higher T_e values of 1.4–5 eV, while maintaining T_g in the range of 1000–6000 K [156]. The ranges of T_g and T_e in these reactors are plotted in Figure 4-1.

Given this diversity, we selected a broad region of investigation that covers a wide range of T_e (0 to 3.5 eV) and T_g (1000 to 6000 K). Note that $T_e = 0$ eV corresponds to pure thermal conditions (without plasma). We believe that this broad domain of our systematic investigation allows us to offer valuable and comprehensive insights into warm plasma NH_3 cracking.

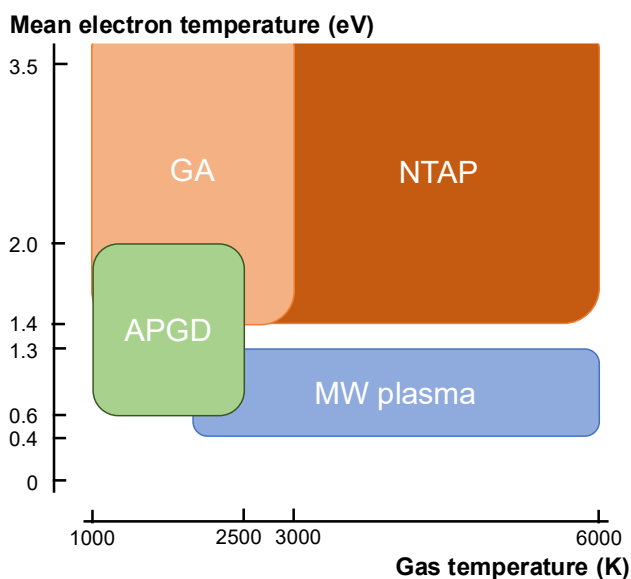


Figure 4-1 - Typical operating conditions of atmospheric pressure warm plasmas: gliding arc (GA) [158], non-thermal arc plasma (NTAP) [165,167], atmospheric pressure glow discharge (APGD) [135,162], and microwave (MW) plasma [159,168,169]. In this chapter, the gas temperature ranges from 1000 to 6000 K and the mean electron temperatures are from 0 to 3.5 eV (corresponding to ca. 40,000 K).

4.2.2 Reaction mechanism

The plasma chemical kinetics reaction mechanism consists of two different reaction parts: (i) a plasma reaction mechanism for the electron-induced chemistry (i.e., electron-impact reactions, but also quenching of excited species, and ion reactions); and (ii) a thermal reaction mechanism for the thermally induced chemistry (i.e., reactions with neutral ground state species governed by the gas temperature).

The plasma reaction mechanism for NH₃ cracking is defined by 39 species (see Table 4-1 below) and 927 reactions with electrons, ions, and excited species. It was compiled from data in the literature and the LXCAT database [59,170]. Again, the full chemical reaction set can be found in the Supporting Information of our paper [171].

We consider 230 electron-impact reactions. For NH₃ and its fragments (i.e., NH₂ and NH), the cross-section data were taken from the theoretical calculation via the R-matrix approach [172], as it is the most complete and latest data set. Cross sections for both H₂ and N₂ electron-impact reactions are taken from the IST Lisbon database, a reliable dataset based on experimental validation. However, cross sections for electron-ion recombination and for electron-impact electronic excitation or ionization of excited species had to be adopted from various sources. Furthermore, 128 ion reactions are incorporated, with their rate coefficients also adopted from the literature. For the excited species (see Table 4-1), 569 quenching reactions are included, but the rate coefficients for the majority (468 reactions) had to be estimated due to limited available data. We believe this is one of the most challenging parts in developing a plasma reaction mechanism. Most of the reactions remain unexplored or were only studied a long time ago under limited conditions, such as low pressure [173] and room temperature [174]. This unavailability may be attributed to the lack of proper measurement tools, but also theoretical studies are very limited. However, considering the fact that such reactions can influence the entire chemical kinetics, in analogy to the O(¹D) reactions in O₃ production [175] and plasma-assisted combustion [176–178], we have to include the excited state reactions in our model. Therefore, we estimated all possible reactions and included them in the plasma reaction mechanism, since we are not limited by computational time in this 0D model. To approximate the rate coefficients for which values are not available in the literature, we reduced the activation energy by the threshold energy of each excited species, assuming an efficiency of 1 for these processes. Furthermore, the reverse processes, i.e., endothermic processes with excited states, have their energy barrier increased to the reaction's endothermic enthalpy. While this

approach may affect accuracy, we believe it provides a reasonable basis to assess the potential significance of these reactions. It should, however, be noted that systematic measurements are required for obtaining more accurate reaction rate coefficients. For the other quenching reactions (i.e., 101 reactions), we used measured collisional quenching rate coefficients for all long-lived excited states and radiative decay rate coefficients for the short-lived excited states.

The thermal reaction mechanism comprises 104 heavy-particle reactions, mostly related to NH_3 pyrolysis and combustion studies. Once again, the thermal set can be found in the Supporting Information of [171]. We considered different chemical structures of diazene, i.e., $\text{trans-N}_2\text{H}_2$ and $\text{cis-N}_2\text{H}_2$ (denoted as tN_2H_2 and cN_2H_2 in the following sections), given their relevance at gas temperatures above ~ 2000 K [47], see Chapter 5. For the thermal reactions, the reverse rate coefficients were obtained via detailed balance. The temperature-dependent enthalpy and entropy of each species were determined using the seven-term NASA polynomials reported by Burcat [102], valid up to 6000 K. These polynomials were also employed to compute the specific heat capacities of the individual species and, subsequently, the mixture heat capacity used for the self-consistent calculation of gas temperature if needed (see Chapter 2).

All chemical species included in the (plasma and thermal) reaction mechanisms are listed in Table 4-1. Note that vibrationally-excited species are excluded from the actual reaction mechanism, because there is typically no vibrational-translational non-equilibrium in warm plasmas due to rapid vibrational-translational relaxation at elevated gas temperature—depopulating the vibrational levels [48,179–181]. However, the electron energy consumption due to vibrational excitation is effectively accounted for in the EEDF calculations.

Table 4-1 - Species included in the plasma and thermal reaction mechanism for warm plasma NH₃ cracking.

species			
	neutral	excited*	charged
electrons			e ⁻
	N ₂	N ₂ (A ³), N ₂ (B ³),	N ₄ ⁺ , N ₃ ⁺ , N ₂ ⁺
N containing	N	N ₂ (C ³), N ₂ (a ¹) N(² D), N(² P)	N ⁺
H containing	H ₂	H(2s), H(2p), H(n=3)	H ₂ ⁺
	H		H ⁺ , H ⁻
	NH ₃ , NH ₂ , NH	NH ₂ (A),	NH ₄ ⁺ , NH ₃ ⁺ , NH ₂ ⁺ ,
N-H containing	N ₂ H ₄ , N ₂ H ₃ , trans-N ₂ H ₂ , cis-N ₂ H ₂ NNH, H ₂ NN	NH(a), NH(b), NH(c), NH(A)	NH ⁺

*The notations for the various excited levels are explained in the literature [48,179–181].

4.2.3 Performance metrics

To analyze the performance of warm plasma NH₃ cracking across all tested operating conditions, we calculated the NH₃ conversion (X_{NH_3} , in %) and corresponding EC (in J.mol⁻¹-NH₃) as follows:

$$X_{NH_3}(\%) = \left(\frac{M_{NH_3,initial} - M_{NH_3,remaining}}{M_{NH_3,initial}} \right) \times 100 \% \quad [84]$$

where $M_{NH_3,initial}$ and $M_{NH_3,remaining}$ are the initial and remaining molarity of NH₃ in mol.m⁻³.

$$EC = \frac{\int_{t_0}^{t_{res}} P_d \times V_r(t) dt}{X_{NH_3} \times M_{NH_3,initial} \times V_{g,initial}} \quad [85]$$

where P_d is the power density in $\text{W}\cdot\text{m}^{-3}$, X_{NH_3} is the unitless conversion, $V_{r,\text{initial}}$ and $V_r(t)$ are the initial gas volume and the gas volume as a function of time (expanding due to heating and reactions, while keeping a constant pressure) in m^3 , t_0 is the starting time of the simulation, fixed at 10^{-10} s, and t_{res} is the residence time, fixed at 10^{-2} s for all simulations, which is indeed typical for warm plasma reactors [107]. The changed reactor volume is included in equation 85 to conserve mass. Increased temperature and dissociation both lead to an increase in volume at constant pressure. When evaluating density variables ($\text{x}\cdot\text{m}^{-3}$), this expanded volume must be accounted for.

4.2.4 Validation of the model

Before applying our model to study warm plasma NH_3 cracking, we first validated our newly compiled thermal reaction mechanism by comparing it to experimental data from Benés et al. for a mixture of 994 ppm NH_3 in Ar (Figure 4-2) [148]. For this purpose, we simulated the thermal NH_3 cracking process (also 994 ppm diluted in Ar, as in the experiments) over a temperature range of 1000 to 1800 K, with residence times varying based on the gas temperature. We also compared our mechanism with two other NH_3 pyrolysis mechanisms from the literature: Mech-1 (Glarborg et al. [47]) and Mech-2 (Alturaifi et al. [182]). Mech-1 includes detailed diazene reactions (tN_2H_2 and cN_2H_2), crucial for accurate modeling at high NH_3 concentrations, while Mech-2 has been shown to agree well with experimental data in the mid- T_g range (2100–3000 K).

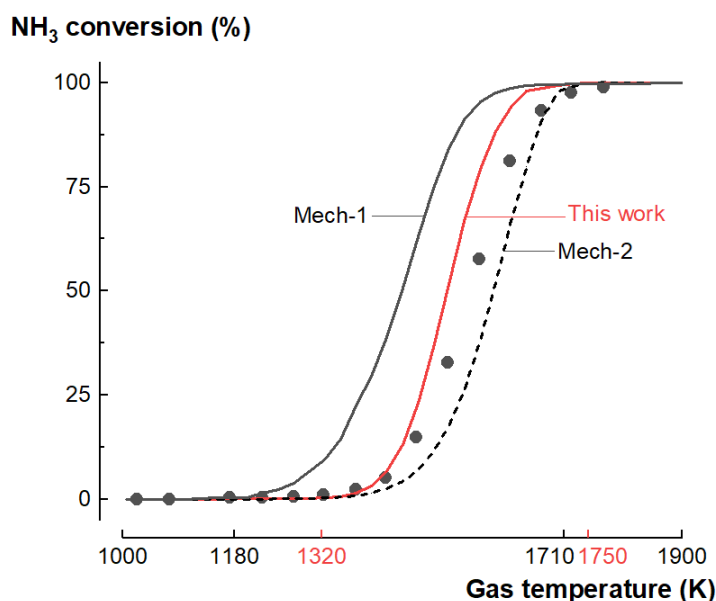


Figure 4-2 - Validation of our newly developed thermal reaction mechanism (red solid line) by comparing with the experimental data from Benés et al. [148] (symbols). The gas temperature is varied from 1000 to 1800 K, and the NH₃ concentration is 994 ppm in Ar. The results from two other reaction mechanisms developed for NH₃ pyrolysis are also presented. Mech-1: solid black line for Glarborg et al. [47], and Mech-2: dashed black line for Alturaifi et al. [182]. The red temperature values indicated on the x-axis correspond to the initiation temperature (1320 K) and the full conversion temperature (1750 K) of the new reaction mechanism (see text).

It is clear from Figure 4-2 that our new thermal reaction mechanism (red solid line) demonstrates improved predictive performance compared to the existing mechanisms. Compared to Mech-1, our new mechanism more precisely captures the initiation temperature of ~1320 K, while Mech-1 predicts that the NH₃ conversion starts earlier at ~1180 K. The slope of the NH₃ conversion is also steeper than that of Mech-1 in our new mechanism, more closely matching the experimental trend. The full conversion temperature is similar to that of Mech-1 (~1710 K for Mech-1 and ~1750 K for our mechanism). When compared to Mech-2, there is no big difference in initiation (~1380 K) or full conversion temperature (~1750 K). However, our new mechanism slightly overestimates the conversion between 1500 and 1700 K, whereas Mech-2 underestimates it. The close agreement of our new mechanism with the experimental data is notable, and the fact that it includes important diazene reactions (not present in Mech-2) suggests that it will probably maintain its accuracy even under pure NH₃.

conditions, where no experimental data is available, to our knowledge, to validate our thermal cracking mechanism.

To the best of our knowledge, no validated plasma reaction mechanism for warm-plasma NH_3 cracking has yet been reported in the literature, and developing such a set remains challenging due to the limited availability of detailed experimental data. Particularly, there are no datasets with accurate measurements of gas and electron temperatures. This lack of precise measurements hinders the comprehensive validation of plasma reaction mechanisms. Most available data primarily provide NH_3 conversion trends as a function of SEI [152,183]. However, these trends can be relatively easily reproduced in models, even with incorrect reaction mechanisms, as they exhibit increasing, often straightforward linear behavior with respect to SEI [184].

To address this limitation, there is growing attention to developing measurement tools for plasma properties in warm plasma chemical processing [185]. Therefore, we hope that systematic measurements and corresponding datasets for model validation will soon become available. For now, however, detailed validation of our plasma reaction mechanism against experimental data is not possible. Furthermore, multidimensional models and experiments have demonstrated that spatial variations in warm plasmas affect the conversion and EC; see Chapters 3 and 5. Hence, it would be incorrect to validate our spatially uniform plasma model by comparing it to contracted arc or microwave reactors, which have distinct flow patterns. Nevertheless, as we will show in section 4.3.1 below, the NH_3 conversion at typical warm plasma conditions is mainly governed by thermal chemistry, which is validated in Figure 4-2 above, so we are confident that our modeling work can provide useful insights into the plasma chemical kinetics of warm plasma NH_3 cracking.

4.3 Results and discussion

The gas temperature (T_g) and mean electron temperature (T_e) affect many characteristics of warm plasma NH_3 cracking, such as the NH_3 conversion and corresponding EC, the final product composition, and the time to reach full conversion. Therefore, in this section, we systematically explore these aspects by simulating plasma NH_3 cracking over a wide range of gas temperatures (1000–6000 K) and mean electron temperatures (0–3.5 eV, where 0 eV corresponds to pure thermal cracking). All simulations assume pure NH_3 as the feed gas. Note that the temperature range covers the typical operating conditions for warm plasmas (cf. section 4.2.1). Because warm plasma reactors often create complex flow patterns—such as swirling, turbulent, and

reverse-vortex flows—and feature steep temperature gradients throughout the reaction zone (inside the reactor), determining the exact residence time is not straightforward. Therefore, we assume a representative value of 10 ms [48,73], but we also tested three shorter residence times: 0.5, 1, and 5 ms.

4.3.1 NH₃ conversion

Figure 4-3 presents the NH₃ conversion as a function of T_e (Figure 4-3a, at constant T_g of 1500 K) and T_g (Figure 4-3b, at fixed T_e of 0.5 eV). It is clear that NH₃ conversion increases with both T_e and T_g , after a certain threshold is reached. This behavior is expected, as a higher T_e and T_g enhances the rates of plasma (electron-induced) reactions and thermal chemical reactions, respectively. In particular, the trend in terms of T_g is not surprising, as it is typical in many chemical processes [186–189].

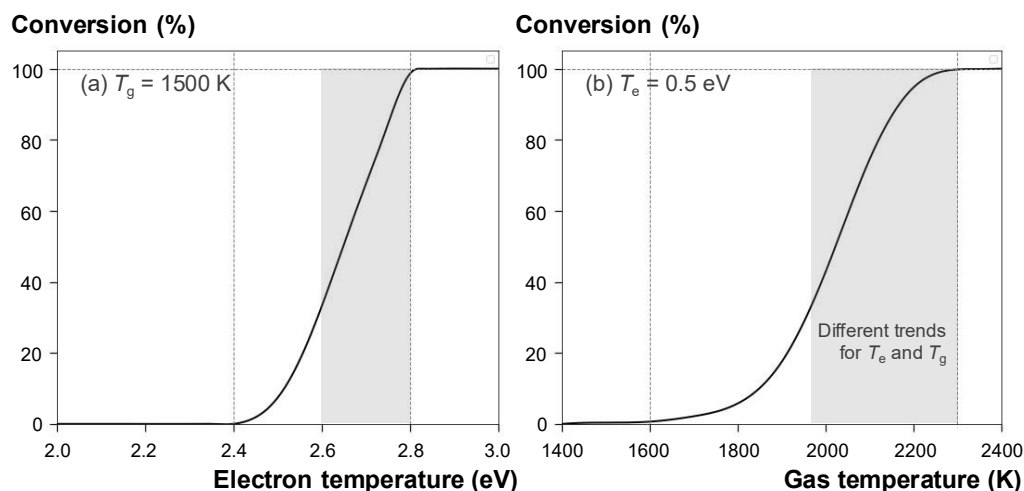


Figure 4-3 - NH₃ conversion as a function of (a) electron temperature (T_e) at fixed $T_g = 1500$ K, and (b) gas temperature (T_g) at fixed $T_e = 0.5$ eV, for a residence time of 10 ms. The shaded areas represent the different trends with respect to T_e and T_g .

However, while the lower conversion trends are very similar, the trends close to full conversion are not the same for T_e and T_g . They act similarly in the way that after the threshold in T_e (ca. 2.4 eV) and T_g (ca. 1600 K), the NH₃ conversion first rises gradually, followed by a linear increase. However, at around 100 % conversion for T_e , slope of conversion drops abruptly, while the slope drops gradually with increasing T_g , from 2100 K, until 100 % conversion is reached at 2300 K. The linear trend with T_e directly results

from the (same) linear rise of specific energy input (SEI) with increasing T_e , and it highlights that the governing mechanism of the T_e effect on NH_3 cracking is the plasma activation mechanism, which exhibits a linear relationship between SEI and target gas conversion [184]. Note that SEI is the ratio of power to gas flow rate and is a common parameter in plasma chemical conversion. The linear trend of conversion with rising T_g up to 2100 K arises from the fact that the rates of thermal NH_3 cracking also rise (more or less) linearly with T_g , and back-reactions (of N_2 and H_2 , back into NH_3) are negligible, while the saturation above 2100 K is a typical behavior when back-reactions start to play a significant role. What is notable, however, is that these back-reactions remain negligible up to a relatively high T_g of 2100 K—unlike in other warm plasma processes such as CO_2 splitting [74,190] and NO_x formation in air plasmas [73,105].

While this observed conversion trend as a function of T_g and T_e always remains consistent for all tested conditions (as shown in Figure 4-4), both temperature parameters can act synergistically to accelerate NH_3 decomposition. For instance, at $T_g = 2100$ K and a residence time (t_{res}) of 10 ms (Figure 4-4d), the conversion remains around 50 % at $T_e < 2.5$ eV, whereas it increases to 80 % and 100 % at $T_e = 2.5$ eV and 2.7 eV, respectively. This finding can be regarded as the plasma-thermal synergy between electron-impact NH_3 dissociation (reactions R1 and R2 in section 4.3.4 below) and thermal dissociation (R3 and R4) (see section 4.3.4 for details of these reactions), however this synergy is confined to a narrow window—approximately 0.5 eV in T_e and 500 K in T_g —regardless of residence time, indicating that the interaction between plasma and thermal pathways remains weak under the examined conditions. If the coupling were more substantial, a much broader transition region would be expected; in that case, significant NH_3 conversion should occur at notably lower gas temperatures (e.g., ~1400 K instead of 2000 K) when the electron temperature approaches 2.5 eV, which is not observed. Outside this range, NH_3 conversion is governed primarily by either plasma or thermal chemistry.

In terms of t_{res} , the onset and full conversion temperatures show markedly different behaviors depending on whether electron temperature (T_e) or gas temperature (T_g) is considered. For T_e , the trend is monotonic: increasing the residence time reduces the required T_e for both onset and full conversion. For example, at $T_g = 1000$ K and $t_{\text{res}} = 0.5$ ms (Figure 4-4a), T_e values of approximately 2.7 eV and 3.4 eV are required to initiate and complete NH_3 conversion, respectively. When t_{res} is extended to 10 ms under the same T_g condition (Figure 4-4d), these thresholds decrease to 2.4 eV for onset and 2.8 eV for full conversion.

Interestingly, the effect of residence time on T_g for onset and full conversion shows a different behavior. While the onset T_g for NH₃ conversion decreases with increasing t_{res} —from 2000 K for 0.5 ms (Figure 4-4a) to 1600 K for 10 ms (Figure 4-4d), resembling the trend observed for T_e —the temperature required for full conversion becomes effectively independent of residence time once t_{res} exceeds 1 ms. For example, full conversion occurs at $T_g = 3000$ K for $t_{res} = 0.5$ ms (Figure 4-4a), but this threshold drops to 2300 K at $t_{res} = 1$ ms (Figure 4-4b) and remains constant at longer residence times (Figure 4-4c for 5 ms and Figure 4-4d for 10 ms).

This invariance in T_g to reach full conversion is attributed to a shift in the dominant thermal decomposition mechanism. Below 2000 K, NH₃ is primarily decomposed via a slow process involving collisions with high-energy neutral species (see R5 in section 4.3.4). Its rate is strongly dependent on temperature and requires longer residence time for significant conversion. In contrast, above 2000 K, the concentration of H radicals increases sharply (exceeding 1% for $t_{res} > 1$ ms), enabling the much faster H-abstraction pathway (R4). This radical-driven pathway becomes dominant above 2000 K, allowing rapid NH₃ decomposition independent of further residence time. The effect is also further amplified by the steep increase in the rate coefficient of R4 at high temperatures. As a result, once the radical pool is sufficiently populated, NH₃ conversion consistently completes at $T_g = 2300$ K, regardless of how long the gas remains in the reactor (at least for the residence times investigated here).

Electron Temperature (eV)

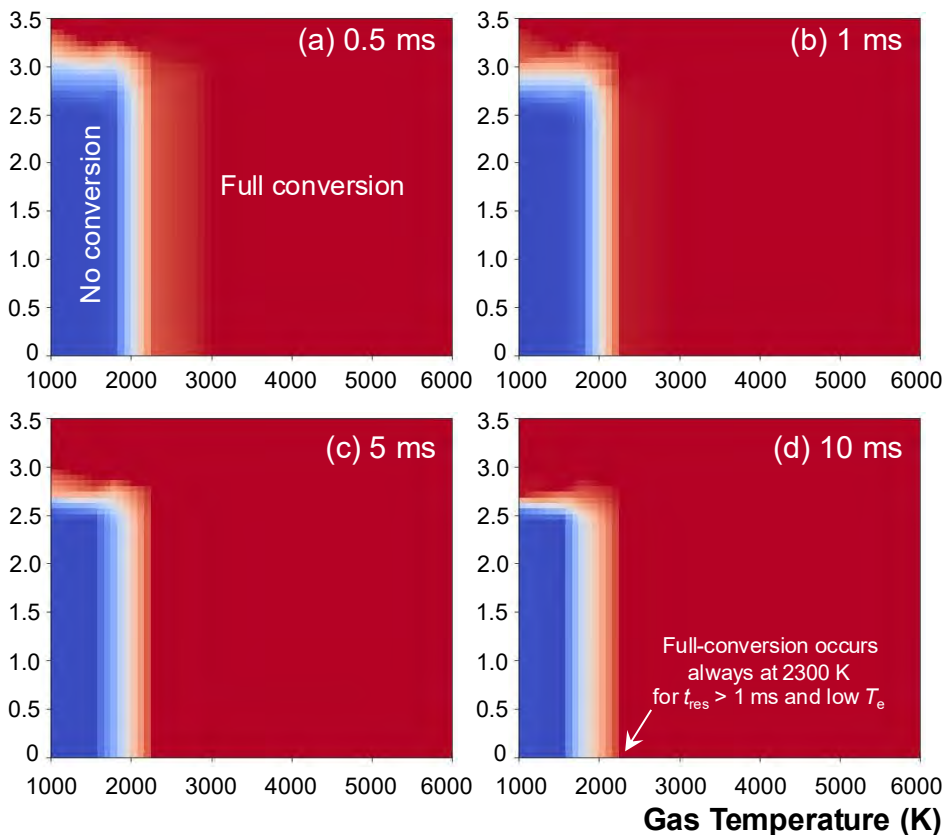


Figure 4-4 - NH_3 conversion at typical atmospheric pressure warm plasma conditions ($T_g = 1000\sim 6000$ K; $T_e = 0\sim 3.5$ eV), for pure NH_3 at a residence time of (a) 0.5, (b) 1, (c) 5 and (d) 10 ms; the latter is representative of typical warm plasma reactor operation [48,73]. Red indicates full conversion, while blue indicates no conversion.

Under typical warm plasma operating conditions ($T_g > 2300$ K), NH_3 can thus be fully converted within typical residence times (even down to ca. 1 ms) regardless of the electron temperature (T_e), as indicated by the wide red region in Figure 4-4b-d. In contrast, for $T_g < 2300$ K, full conversion only occurs when T_e is sufficiently high—typically above 2.5–3 eV (depending on residence time). This behavior is due to the initial decomposition of NH_3 into NH_2 and H being rate-limiting under these conditions.

4.3.2 Final product composition

To investigate the influence of T_g and T_e on the time evolution of species formation, and on the final NH_3 cracking products, we plot in Figure 4-5 the mole fractions of the major

products as a function of time, for six different operating conditions, based on three different gas temperatures ($T_g = 1500, 3000, \text{ and } 6000 \text{ K}$) and two mean electron temperatures ($T_e = 0.5 \text{ and } 3.5 \text{ eV}$). Note that Figure 4-5 only shows the neutral species. Charged species are excluded due to their rapid decay and fast reaction rates, even though their impact on the reaction kinetics can be significant. On the other hand, some excited species, like $\text{N}(^2\text{D})$, $\text{NH}_2(\text{A})$, and $\text{NH}(\text{A})$, are still present, as their radiative lifetimes are about 10 hours, 10 μs , and 500 ns, respectively, so they are called metastable excited species.

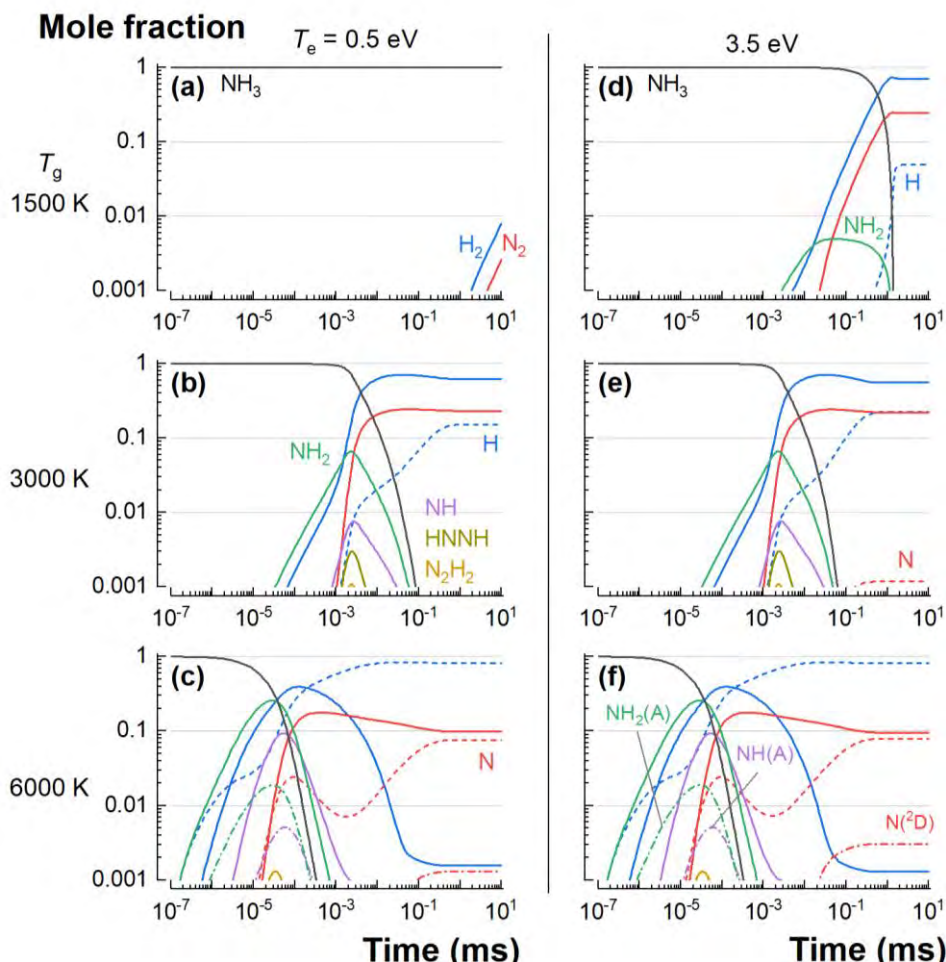


Figure 4-5 - Time evolution of the mole fractions of the major neutral species for pure NH₃ cracking, at: (a) $T_g = 1500 \text{ K}$; $T_e = 0.5 \text{ eV}$, (b) 3000 K ; 0.5 eV , (c) 6000 K ; 0.5 eV , (d) 1500 K ; 3.5 eV , (e) 3000 K ; 3.5 eV , (f) 6000 K ; 3.5 eV . For clarity, the N and H atoms are plotted with dashed lines, and the excited species with dash-dotted lines.

The final products, as well as the time evolutions, are clearly dependent on T_g . Roughly speaking, the final product composition is primarily governed by thermal equilibrium, which shifts with T_g . Indeed, as thermal equilibrium shifts from NH_3 to the neutral molecules (N_2 and H_2) and further to the corresponding atoms (N and H) upon increasing T_g , the final products of NH_3 cracking contain more H and N atoms at higher T_g (Figure 4-5a to Figure 4-5c). At low T_g of 1500 K and low T_e of 0.5 eV (Figure 4-5a), NH_3 is barely decomposed into N_2 and H_2 within the residence time of 10 ms, which clearly illustrates that the thermal equilibrium composition is not yet reached at this timescale, for pure thermal conversion. Upon increasing T_g to 3000 and 6000 K, the time to initiate conversion is around 500 ns and 1 ns, respectively, while full conversion (NH_3 mole fraction < 0.001) is achieved at 100 μs and 1 μs (cf. Figure 4-5b and Figure 4-5c). Hence, the thermal equilibrium composition is reached well within the residence time of 10 ms. In addition, at $T_g = 3000$ K (Figure 4-5b), the H_2 molecules are partially dissociated into H atoms, which constitute a molar fraction of 0.15 of the gas mixture. Furthermore, at T_g of 6000 K (Figure 4-5c), N_2 also begins to dissociate into N atoms, reaching a mole fraction of 0.08, while the N_2 mole fraction is only slightly higher (0.10). In contrast, at this high temperature, all H_2 molecules are converted into H atoms (H atom mole fraction close to 1).

At $T_g = 3000$ and 6000 K, the effect of T_e is minor, except for some slight changes in mole fraction of the H atoms at $T_g = 3000$ K (cf. Figure 4-5e vs. Figure 4-5b) and of the N atoms at $T_g = 6000$ K (cf. Figure 4-5f vs. Figure 4-5c), attributed to electron-impact dissociation of H_2 and N_2 ($\text{e} + \text{H}_2 \rightarrow \text{e} + \text{H} + \text{H}$, and $\text{e} + \text{N}_2 \rightarrow \text{e} + \text{N} + \text{N}$, respectively).

On the other hand, the effect of T_e is quite dominant at $T_g = 1500$ K (cf. Figure 4-5d vs. Figure 4-5a). At low $T_e = 0.5$ eV (Figure 4-5a), at which plasma (electron-induced) reactions are not yet important, nearly no NH_3 conversion is observed within 10 ms. However, at $T_e = 3.5$ eV, NH_3 cracking starts at 10 μs and is complete at 1 ms (Figure 4-5d). Hence, the plasma reactions drastically reduce the time to initiate conversion, and full conversion is reached within the typical residence time of 10 ms.

4.3.3 Time to reach full conversion

The time required to achieve full NH_3 conversion is illustrated in Figure 4-6 as a function of gas temperature (T_g), comparing pure thermal conversion ($T_e = 0$ eV) with warm plasma-assisted conversion ($T_e = 3.5$ eV). The results clearly demonstrate the significant enhancement in reaction kinetics enabled by plasma. For instance, at $T_g = 1100$ K, plasma-assisted NH_3 decomposition reduces the full conversion time from

approximately 3600 years to just 3 ms. Similarly, at $T_g = 1500$ K, the conversion time decreases from around 10 hours to 2 ms.

Meanwhile, as T_g increases, the difference in conversion time between plasma-enhanced and purely thermal pathways diminishes. At $T_g = 2000$ K, full conversion is achieved thermally within 0.5 s, and this is further reduced to 900 μ s under plasma conditions. At $T_g = 3000$ K, the conversion time converges to approximately 78 μ s regardless of plasma input. Above 2700 K, plasma effects become negligible, and NH₃ decomposition proceeds almost exclusively via thermal reaction pathways.

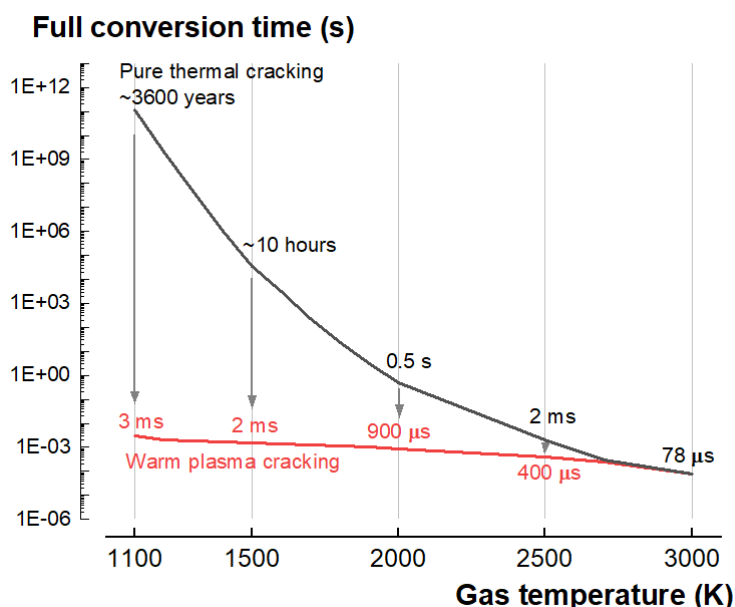


Figure 4-6 - Time to reach full conversion, for pure thermal cracking (black line) and for warm plasma cracking at $T_e = 3.5$ eV (red line), as a function of gas temperature, for pure NH₃. At $T_g = \sim 2700$ K, both cracking processes need ~ 200 μ s to reach full conversion, indicating that thermal chemistry becomes dominant at higher temperatures.

4.3.4 Underlying chemistry governing the NH₃ conversion

The previous sections demonstrate that warm plasma NH₃ cracking is significantly affected by changes in T_e and T_g . Since these changes are directly governed by the underlying chemical mechanisms, which depend on T_e and T_g , conducting a detailed chemical analysis helps to understand the changes in conversion performance.

To address this, we integrated the calculated reaction rates over the simulated residence time to identify the essential reaction pathways in warm plasma NH_3 cracking (Figure 4-7 and Table 4-2). Figure 4-7 schematically illustrates the plasma reaction route (i.e., through electron-impact) and the two primary thermal NH_3 decomposition pathways (i.e., the NH_x route and the N_2H_x route), while Table 4-2 lists all these key reactions. A detailed reaction pathway analysis at the six distinct operating conditions of Figure 4-5 (i.e., three different values of T_g and two different T_e values), as well as their specific contributions to individual species losses, can be found in the supporting information of the paper this chapter is based on [171].

Main routes for warm plasma cracking

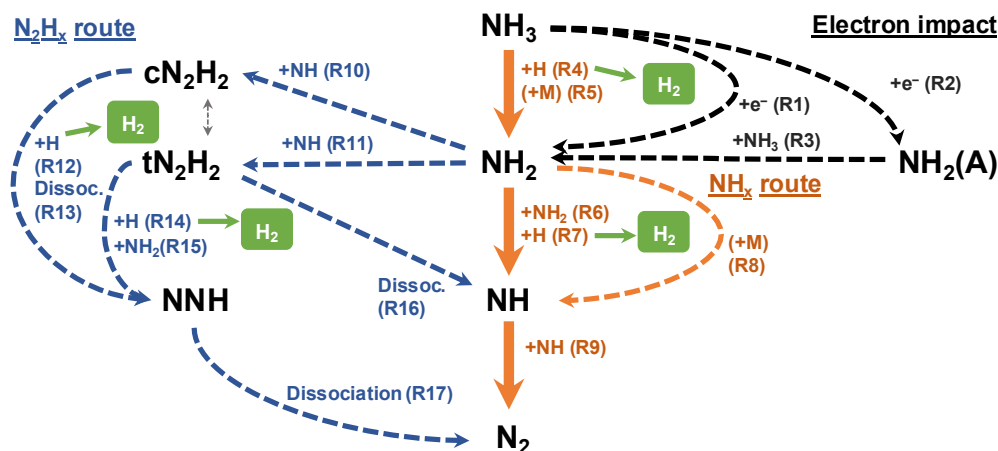


Figure 4-7 - Main reaction routes for warm plasma NH_3 cracking across the entire range of T_e (0–3.5 eV) and T_g (1000–6000 K). The plasma reaction through electron-impact reactions is indicated by black dashed arrows, the NH_x route by orange arrows, and the N_2H_x route by blue arrows. The solid arrows are important in the entire range of investigated conditions, while the dashed arrows are important in the low- and mid- T_g range (1000–4000 K). Reactions R4, R7, R12, and R14 yield the formation of H_2 , indicated in green rectangles.

Table 4-2 - List of main reactions in warm plasma NH₃ cracking and corresponding contribution to loss of the main reactant (NH₃ or one of the radicals leading to N₂ and H₂), within the range of typical operating conditions ($T_e = 0\sim 3.5$ eV and $T_g = 1000\sim 6000$ K).

#	Reaction	Contribution (%) to loss of the main reactant*
Electron-impact reactions (significant at low $T_g < 2700$ K and high $T_e > 2.5$ eV)		
(R1)	$e^- + \text{NH}_3 \rightarrow e^- + \text{NH}_2 + \text{H}$	14
(R2)	$e^- + \text{NH}_3 \rightarrow e^- + \text{NH}_2(\text{A}) + \text{H}$	12
Relaxation of excited state		
(R3)	$\text{NH}_2(\text{A}) + \text{NH}_3 \rightarrow \text{NH}_2 + \text{NH}_3$	
NH_x route		
(R4)	$\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$	53–85
(R5)	$\text{NH}_3 (+\text{M}) \rightarrow \text{NH}_2 + \text{H} (+\text{M})$	0–47
(R6)	$\text{NH}_2 + \text{NH}_2 \rightarrow \text{NH} + \text{NH}_3$	8–46
(R7)	$\text{NH}_2 + \text{H} \rightarrow \text{NH} + \text{H}_2$	18–40
(R8)	$\text{NH}_2 (+\text{M}) \rightarrow \text{NH} + \text{H} (+\text{M})$	0–16
(R9)	$\text{NH} + \text{NH} \rightarrow \text{N}_2 + \text{H} + \text{H}$	5–23
N₂H_x route		
(R10)	$\text{NH}_2 + \text{NH} \rightarrow \text{cis-N}_2\text{H}_2 + \text{H}$	4–14
(R11)	$\text{NH}_2 + \text{NH} \rightarrow \text{trans-N}_2\text{H}_2 + \text{H}$	14–47
(R12)	$\text{cis-N}_2\text{H}_2 + \text{H} \rightarrow \text{NNH} + \text{H}_2$	58–98
(R13)	$\text{cis-N}_2\text{H}_2 \rightarrow \text{NNH} + \text{H}$	0–38
(R14)	$\text{trans-N}_2\text{H}_2 + \text{H} \rightarrow \text{NNH} + \text{H}_2$	0–73
(R15)	$\text{trans-N}_2\text{H}_2 + \text{NH}_2 \rightarrow \text{NNH} + \text{NH}_3$	0–27
(R16)	$\text{trans-N}_2\text{H}_2 \rightarrow \text{NH} + \text{NH}$	0–57
(R17)	$\text{NNH} \rightarrow \text{N}_2 + \text{H}$	100

*The range in contributions in the last column corresponds to the range of typical operating conditions ($T_e = 0\sim 3.5$ eV and $T_g = 1000\sim 6000$ K); the detailed contributions for

the six distinct conditions (cf. Figure 4-5) can be found in the supporting information of the paper this chapter is based on [171].

Based on our chemical analysis, we can identify four key aspects of the underlying chemistry of warm plasma NH_3 cracking. These aspects are directly linked to the observed NH_3 conversion, final product composition, and the time required to achieve full conversion:

First, main reactions: A total of 17 reactions (14 thermal and 3 plasma reactions) are identified as important for warm plasma NH_3 cracking across the entire operating range, as summarized in Table 4-2.

Second, role of plasma reactions: Electron-impact reactions (R1 and R2 in Table 4-2, black dashed arrows in Figure 4-7) are important, particularly for T_g up to 2700 K. These reactions not only initiate the cracking process, but also produce abundant H atoms, which facilitate thermal reactions, like R4. These two aspects significantly shorten the time to reach full conversion (Figure 4-6) and are also responsible for the reduction in initiation and full conversion temperature in Figure 4-4. Thus, optimizing plasma conditions is important for efficient NH_3 cracking at low T_g . The sum of the contributions of R1 and R2 to NH_3 loss is about 26%, for $T_g < 2700$ K and $T_e > 2.5$ eV. Other plasma reactions are virtually negligible; the only other notable reaction is simple $\text{NH}_2(\text{A})$ relaxation to NH_2 upon collision with NH_3 (R3), and the other excited species have mole fractions below 0.01 (Figure 4-5).

Third, major reaction scheme: Regardless of T_e (at least for $T_g > 1800$ K, but only at higher T_e for lower T_g), warm plasma NH_3 cracking proceeds by the following two primary routes, both initialized by H production upon R1, R2, and R5:

- (i) NH_x route: $\text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{NH} \rightarrow \text{N}_2$ (R4–R9 in Table 4-2, and orange arrows in Figure 4-7), dominant across the entire T_g range, and more and more significant upon rising T_g . Of these reactions, R4 and R7 create H_2 .
- (ii) N_2H_x Route: $\text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{trans-N}_2\text{H}_2$ or $\text{cis-N}_2\text{H}_2 \rightarrow \text{NNH} \rightarrow \text{N}_2$ (R10–R17 in Table 4-2, and blue arrows in Figure 4-7), prevalent up to T_g of ~ 4000 K, but insignificant at high T_g of 6000 K. Of these, R12 and R14 produce H_2 .

Fourth, effect of H-abstraction: The H-abstraction reactions (R4, R7, R12, and R14 in Table 4-2) are the primary drivers of H_2 production, as 98–99.5 % of H_2 is produced from these channels, rising with T_g . They are particularly important because of their strong T_g -dependence, with rapid increase in reaction rates at high T_g due to their endothermic

nature, leads to a sharp rise in NH₃ conversion above 2000 K (Figure 4-3 and Figure 4-4) and an exponential reduction in the time to reach full conversion of pure thermal cracking (Figure 4-6). Note that these reaction rate coefficients are independent of T_e .

As the final stage of this study, we evaluate the EC under typical warm plasma-based NH₃ cracking conditions, as the primary performance metric, and we explore potential strategies to enhance energy efficiency. The objective is to translate the observed trends—such as the dominance of thermal pathways, the limitations of electron-impact reactions, dramatic kinetic enhancements, and the underlying chemistry—into actionable strategies to improve reactor operation and design.

4.3.5 EC of NH₃ cracking at typical operating conditions

To reflect the typical operating mode of warm plasma reactors—where the gas temperature is not externally controlled but instead calculated from the supplied power—we performed the first set of EC simulations using a continuous power input, defined by a fixed power density (P_d). In this configuration, the gas temperature (T_g) evolves self-consistently due to energy input and chemical reactions. This modeling approach captures the chemical behavior of most warm plasma reactors, though idealized, operating at high current and elevated gas temperatures (above 2000 K), such as gliding arc (GA), non-thermal arc plasma (NTAP), and microwave (MW) plasmas (see section 4.2.1), and provides a reference point for developing strategies to improve energy efficiency in the next sections.

Figure 4-8 presents the EC, calculated using equation 85 in section 4.2.3, as a function of the plasma processing time, ranging from 0.5 to 10 ms. The power density, which is used to calculate EC (cf. equation 85), is varied as follows (13 different conditions, each represented by a distinct line): $P_d = 1 \times 10^8, 1.25 \times 10^8, 1.55 \times 10^8, 1.75 \times 10^8, 2.1 \times 10^8, 2.5 \times 10^8, 2.9 \times 10^8, 3.5 \times 10^8, 4.5 \times 10^8, 5.5 \times 10^8, 7.5 \times 10^8, 9.5 \times 10^8, 1.15 \times 10^9$ W.m⁻³ (with the first line corresponding to the highest P_d , and the last one to the lowest P_d). The color scale along each line indicates the NH₃ conversion (Figure 4-8a) and T_g (Figure 4-8b) as they evolve over time. Note that the residence time begins at 0.5 ms, as a minimum level of NH₃ conversion (a few ppm) is required for EC to be calculated.

Across all P_d cases, the EC initially rises as a function of time, to values in the thousands of kJ.mol⁻¹-NH₃ at low NH₃ conversion, then decreases to the range of a few hundred as conversion progresses, ultimately reaching the minimum EC at full conversion (as indicated by the lowest EC values when the various lines reach red color in Figure 4-8a).

After full conversion is achieved, the EC increases sharply, exceeding values in the tens of thousands of $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{NH}_3$. This sharp rise results from the fact that additional power input no longer contributes to chemical transformation (as full conversion is reached already) but instead leads to excessive gas heating (see line colors in Figure 4-8b) or the dissociation of reaction products—primarily H_2 into H atoms (illustrated in Figure 4-5). However, the latter energy penalty can be regarded as part of the overall overheating effect, since the energy consumed for H_2 dissociation is released again when H radicals recombine during gas cooling. Thus, the excess energy is not irreversibly lost but is instead temporarily stored as chemical potential energy and recovered upon cooling.

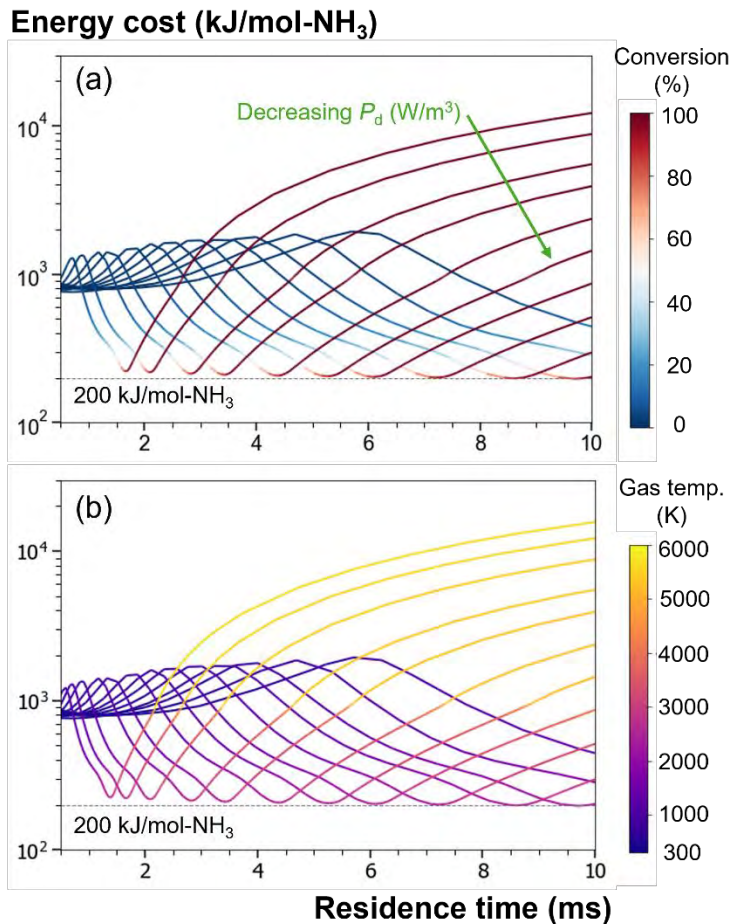


Figure 4-8 - EC as a function of residence time (t_{res}), for 13 different conditions of power density (each represented by a distinct line, with the first line corresponding to the highest power density): $P_d = 1 \times 10^8$, 1.25×10^8 , 1.55×10^8 , 1.75×10^8 , 2.1×10^8 , 2.5×10^8 , 2.9×10^8 , 3.5×10^8 , 4.5×10^8 , 5.5×10^8 , 7.5×10^8 , 9.5×10^8 , $1.15 \times 10^9 \text{ W}\cdot\text{m}^{-3}$. Line colors indicate the corresponding (a) NH_3 conversion and (b) gas temperature.

Two remarkable observations can be made. First, the minimum EC for all power density (P_d) conditions—corresponding to the point of reaching full NH₃ conversion—occurs at a similar gas temperature (T_g) of 2500–2700 K (Figure 4-8b). Although electron-impact reactions become more prominent at higher P_d , full conversion consistently takes place at comparable T_g values, where the H-abstraction reaction (R4) is highly active, as also shown in Figure 4-4. This indicates that electron-impact decomposition is not the dominant pathway in most warm plasma reactors. Instead, electrons primarily serve to excite stable molecules such as NH₃, H₂, and particularly N₂ into vibrational or electronic states. As these excited species relax, they transfer energy to the gas, raising T_g . Once T_g becomes sufficiently high, thermal reactions take over, and NH₃ decomposition proceeds through conventional high-temperature kinetics—most notably via R4, as detailed in section 4.3.4 above.

Second, the minimum EC slightly decreases with lower power density (P_d) and correspondingly longer residence time—from 224 kJ.mol⁻¹-NH₃ at 1.2 ms for 1.15×10^9 W.m⁻³ to 197 kJ.mol⁻¹-NH₃ at 9.6 ms for 1.55×10^8 W.m⁻³. This trend is attributed to the role of H radicals produced via R5. Under high P_d conditions, the gas temperature increases rapidly, and electron-impact reactions (such as R1 and R2) dominate, leading to rapid NH₃ depletion. As a result, H radicals have little time to encounter remaining NH₃ molecules and instead tend to recombine into H₂, releasing stored energy as heat. However, this heat no longer contributes to NH₃ cracking, as most of the NH₃ is already decomposed. In contrast, at lower P_d , the heating rate is slower, and NH₃ is consumed more gradually. This extended timeframe allows a greater fraction of H radicals to react with NH₃ via R4 rather than recombining into H₂. Furthermore, radicals at lower gas temperatures tend to recombine rather than drive further decomposition reactions; see section 4.3.7. Consequently, the available chemical energy is used more effectively for cracking, resulting in a lower overall EC.

4.3.6 EC of NH₃ conversion at constant gas temperatures

To isolate the effects of continuous power input, we performed additional simulations at constant gas temperature. This approach prevents excessive energy consumption due to overheating beyond full conversion and decouples thermal kinetics (with T_g held fixed) from electron-impact kinetics. The reported EC in these simulations corresponds to the lowest value attained at any point during the simulation. To ensure comparability with the above self-consistent simulations (as defined by equation 85), the EC was calculated by considering three energy contributions: (i) the energy required to raise the NH₃ feed

from room temperature (300 K) to the setpoint temperature (see Chapter 2), (ii) the energy needed to maintain that temperature in the presence of endothermic and exothermic reactions, and (iii) the energy transferred from electrons to the gas through collisions with heavy species, essentially being the enthalpy difference of the heavy species subtracted from the electron energy loss.

The resulting calculated minimum EC values are presented in Figure 4-9 as a function of SEI, which corresponds to different power density (P_d) conditions. We selected eight gas temperatures ($T_g = 1000$ – 3500 K; shown in different colors in Figure 4-9) within the effective operating window. It should also be noted that each T_g condition has data for thirteen SEI values (with power going only to electrons here), which corresponds to the same P_d conditions as in Figure 4-8.

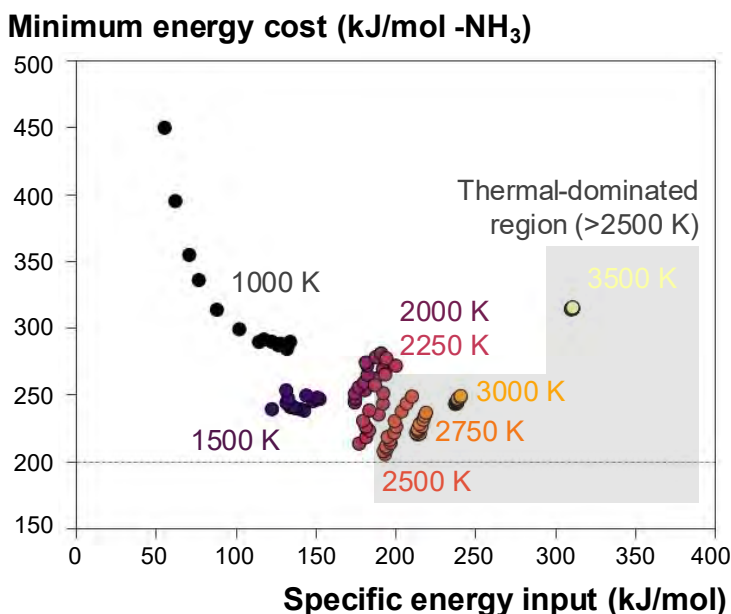


Figure 4-9 - Minimum energy cost (EC) obtained for 13 power densities ($P_d = 1 \times 10^8, 1.25 \times 10^8, 1.55 \times 10^8, 1.75 \times 10^8, 2.1 \times 10^8, 2.5 \times 10^8, 2.9 \times 10^8, 3.5 \times 10^8, 4.5 \times 10^8, 5.5 \times 10^8, 7.5 \times 10^8, 9.5 \times 10^8, 1.15 \times 10^9$ W.m⁻³; represented by symbols in the same color) and eight gas temperatures ($T_g = 1000, 1500, 2000, 2250, 2500, 2750, 3000$, and 3500 K, represented by different colors). Variations in P_d at constant T_g are represented by different SEI values: at a given T_g , higher SEI corresponds to higher input P_d .

Although the fixed-temperature cracking process eliminates the inefficiencies of post-conversion overheating, the results in Figure 4-9 reveal that EC remains bound, with a minimum of approximately $200 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{NH}_3$. At the lowest P_d (i.e., $1.0 \times 10^8 \text{ W} \cdot \text{m}^{-3}$),

where conversion is driven almost purely by thermal reactions, the EC is the highest at $T_g = 1000$ K (450 kJ.mol⁻¹-NH₃) but decreases steadily with increasing gas temperature, reaching a minimum of 200 kJ.mol⁻¹-NH₃ at 2500 K. Notably, beyond this point, the EC no longer decreases; instead, it begins to rise again to 320 kJ.mol⁻¹-NH₃ at $T_g = 3500$ K, highlighting the importance of appropriate T_g selection.

Increasing P_d , thereby enhancing the role of electron-impact NH₃ dissociation, also does not lead to further EC reduction. At low T_g (e.g., 1000 K), the EC initially drops as P_d increases, reflecting the contribution of electron-impact dissociations of NH₃ (R1 and R2) in the absence of sufficient thermal NH₃ dissociation (R5). However, this benefit eventually saturates, with EC plateauing near 290 kJ.mol⁻¹-NH₃—suggesting an intrinsic efficiency limit for electron-impact processes, likely linked to the high energy required for direct NH₃ dissociation by electrons (5.3 eV) [172]. In contrast, at T_g above 2000 K, promoting electron-impact dissociations causes EC to rise. For example, at $T_g = 2500$ K, the minimum EC of 200 kJ.mol⁻¹-NH₃ at low $P_d = 1.55 \times 10^8$ W.m⁻³ increases to 250 kJ.mol⁻¹-NH₃ at high $P_d = 1.15 \times 10^9$ W.m⁻³. This suggests that, although electron-induced pathways are kinetically favorable, their lower energy efficiency compared to thermal routes can result in suboptimal overall energy performance when they dominate the conversion mechanism. The EC is interestingly insensitive to P_d at $T_g = 3000$ K and 3500 K, where thermal reaction kinetics are sufficiently fast to outweigh the influence of electron-induced processes (see Figure 4-6 for $T_g > 2700$ K). This indicates that the optimal EC is achieved when electron-impact reactions are unimportant.

4.3.7 Optimization strategies for EC improvement

Our calculations predict that warm plasma NH₃ cracking at constant gas temperature (i.e., without overheating at maximum conversion) exhibits a lower bound in EC, around 200 kJ.mol⁻¹-NH₃. Even artificially increasing the concentration of H radicals—motivated by their key role in promoting NH₃ dissociation via reaction R4, as shown in section 4.3.4—did not reduce the EC below this threshold. These limitations suggest that further optimization of EC requires a deeper understanding of how the supplied energy is partitioned among various reaction pathways.

To this end, we selected the lowest-EC case at each T_g condition in our constant- T_g simulations (Figure 4-9), and we decomposed that EC into six contributions for six distinct energy channels: four channels considering electron-impact reactions, so: (i) elastic collisions, (ii) vibrational excitations, (iii) electronic excitations and (iv) ionization, heavy species reaction contributions include: (v) initial gas heating, which is the energy

required to heat the initial NH_3 mixture from room temperature to the target T_g , and (vi) thermal energy required to maintain the constant T_g . The selected EC and the contribution of each energy channel are plotted in Figure 4-10.

The energy contributions at high temperatures ($T_g > 2500$ K) confirm that the most energy-efficient NH_3 cracking occurs via purely thermal mechanisms. In this regime, 95–100% of the input energy is consumed for both heating the gas to the target temperature (orange bars in Figure 4-10) and maintaining it during the reaction (yellow bars). This trend reflects a fundamental efficiency limit imposed by thermally equilibrated reaction pathways, where the input energy is inevitably distributed across all degrees of freedom. As a result, there is no remaining opportunity for further EC reduction at high initial temperatures.

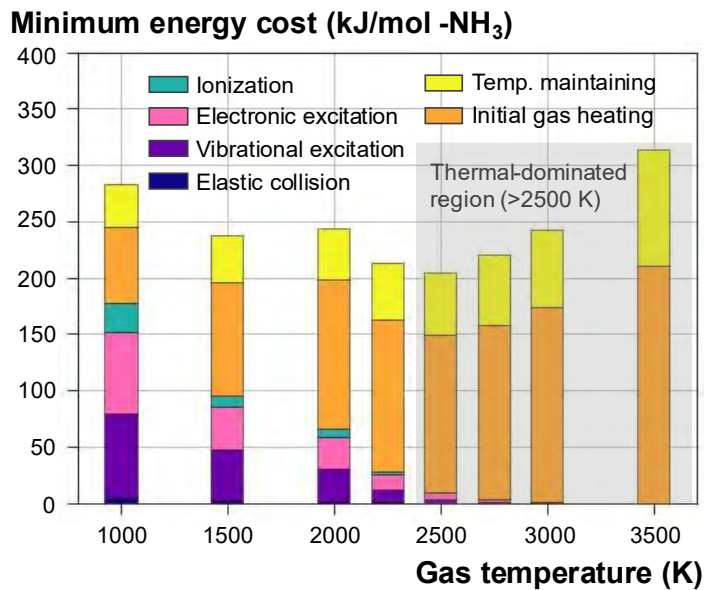


Figure 4-10 - Energy consumption distributions for the best EC case under various gas temperatures (T_g).

Six channels are considered: (i) elastic collisions (dark blue bar), (ii) vibrational excitation (purple), (iii) electronic excitation (including dissociation, pink), (iv) ionization (cyan), (v) heating from 300 K to the set T_g (orange), and (vi) maintaining the set T_g (yellow). Conditions at $T_g > 2500$ K clearly show the dominance of both thermal pathways (temperature initiation and maintaining), whereas the 1500 K case highlights potential for lower EC by eliminating vibrational excitation losses.

At lower temperatures ($T_g < 2500$ K), however, selective energy utilization still offers a pathway to surpass this thermal limit. This is a widely discussed advantage of non-equilibrium plasma operation, in which input energy can be preferentially channeled into specific reactions [17]. For instance, at $T_g = 1000$ K and 1500 K, 27% and 19% of the

energy input, respectively, is lost to vibrational excitations. Theoretically, vibrational excitation, followed by vibrational-vibrational relaxations (i.e., so-called vibrational pumping dissociation or vibrational ladder climbing), can lead to more efficient dissociation, as discussed in the literature for plasma-based CO₂ conversion and NO_x production from air plasmas [15,17]. Yet at elevated temperatures (including already T_g of 1000 K), vibrational excitations primarily relax into heat via rapid vibrational-translational relaxation, rather than driving the theoretically efficient vibrational-pumping dissociation. To address this inefficiency, we propose shifting electron-impact energy deposition away from vibrational modes and toward electronic excitation channels, which are more directly linked to bond dissociation.

This newly proposed approach is theoretically promising, as it offers the potential to achieve lower EC than in warm plasmas (around 200 kJ.mol⁻¹-NH₃, as predicted by our calculations, although experimentally slightly lower values were demonstrated at specific conditions [152]) and also remarkably lower than the experimentally obtained EC in a room temperature plasma reactor of 511 kJ.mol⁻¹-NH₃ [191].

We study this hypothesis in more detail in Figure 4-11, which presents the calculated NH₃ conversion and gas temperature as a function of residence time for the so-called “plasma-initialized” thermal cracking process. We consider four different initial gas compositions (0, 10, 20, and 30% conversion) resulting from initial plasma cracking (without vibrational excitation), and then proceed with purely thermal simulations at two initial gas temperatures, i.e., 300 and 1400 K. The numbers next to the curves in Figure 4-11a and Figure 4-11c indicate the EC reached.

As an example, in an idealized scenario where plasma acts solely as an initiator—generating high concentrations of NH₂ and H radicals, potentially via electron-impact dissociation of R1—the resulting radical pool initiates thermally driven reactions that rapidly raise the gas temperature. For instance, initializing a partially dissociated NH₃ mixture with 20% conversion at $T_g = 1400$ K (purple lines in Figure 4-11) leads to complete NH₃ decomposition at 10 ms (Figure 4-11c), while the gas temperature increases to 1940 K (Figure 4-11d). In this case, the EC consists of two components: the energy required to heat the gas to 1400 K, costing 54.5 kJ/mol for pure NH₃, and the energy required to create the “plasma-initialized” mixture with NH₃, NH₂, and H, yielding a total EC of only 157 kJ/mol-NH₃ (Figure 4-11c). Note that this curve provides the lowest EC, while the other cases presented in Figure 4-11 (based on other initial gas compositions and/or other T_g) yield (much) higher EC. Herein, it is important to note that

NH_3 dissociation into NH_2 and H via electron-impact is highly energy-intensive, while the subsequent thermal reactions among these radicals are exothermic. Therefore, supplying electron energy to form these reactive intermediates can effectively "seed" a chain of thermally driven reactions, potentially achieving full conversion at reduced EC.

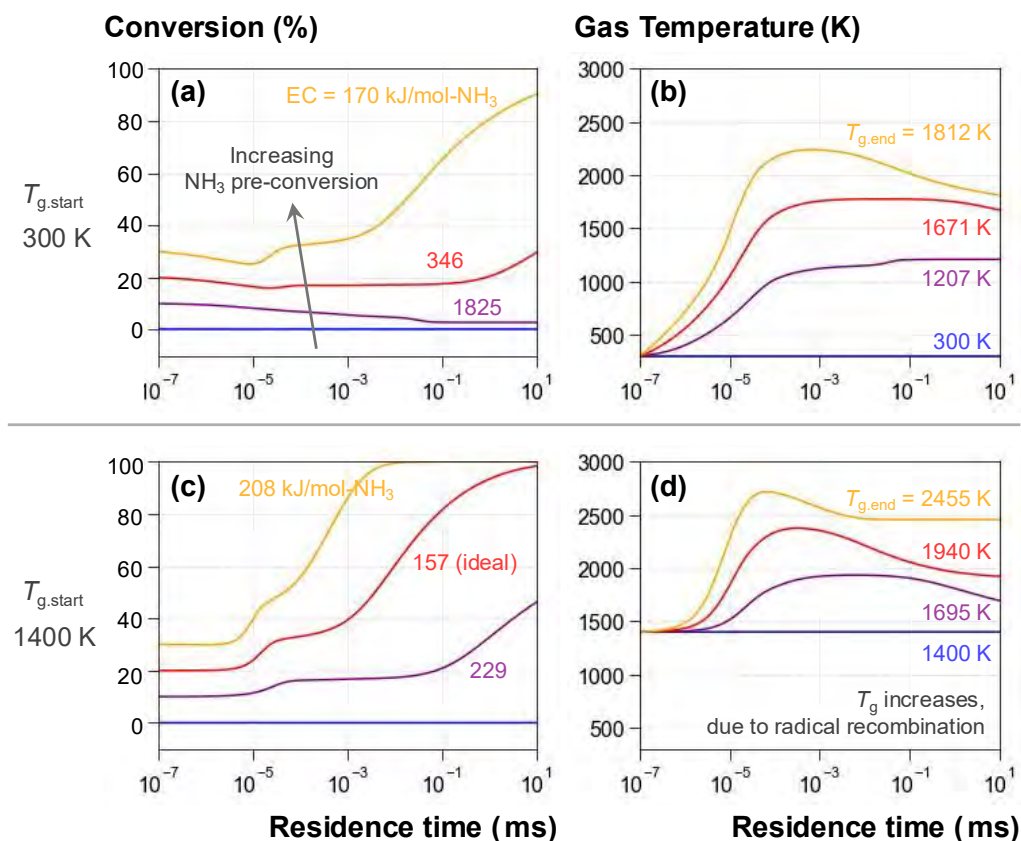


Figure 4-11 - NH_3 conversion (a, c) and gas temperature (b, d) as a function of residence time, for the "plasma-initialized" thermal cracking process. Initial gas compositions (0, 10, 20, and 30% conversion; represented by blue, purple, red, and yellow lines) are assumed to result from an effective plasma-cracking stage. Purely thermal simulations are then conducted at two different initial gas temperatures: 300 K (a, b) and 1400 K (c, d). The numbers written in the same colors as the curves in (a) and (c) indicate the corresponding EC reached.

Previous work by Bayer et al. [191] investigated cold plasma cracking of NH_3 and concluded that the process is theoretically inefficient due to the recombination of NH_2 and H radicals, which limits net NH_3 conversion—a finding consistent with our results

(blue line in Figure 4-11a). However, our simulations reveal that increasing the gas temperature—either by generating a high initial dissociation fraction, such that radical recombination heats the gas (Figure 4-11a and Figure 4-11b), or by preheating the feed to 1400 K (Figure 4-11c and Figure 4-11d)—can drive the conversion beyond the initial dissociation fraction. At elevated temperatures (Figure 4-11c), radicals preferentially promote further NH₃ decomposition rather than recombining. This is evident from the temperature dependence of the relevant rate coefficients: the ratio of the H-abstraction rate (R4) to the high-energy neutral impact rate (R5) increases from 7.31×10^{-11} at 300 K to 1.08×10^{-3} at 1400 K—an enhancement of seven orders of magnitude—highlighting the growing dominance of R4 (i.e., $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$) at higher temperatures. In essence, H radicals generated at room temperature do not contribute to the NH₃ cracking because they predominantly recombine with NH₂; however, at elevated gas temperatures, they play a significant role in promoting decomposition.

However, it is important to recognize that achieving such a “plasma-initialized” thermal cracking scenario remains practically challenging, and our calculations provide only a minimum theoretical EC for this system. In particular, selectively inducing electron-impact dissociation is currently beyond the capabilities of conventional plasma control.

Nevertheless, several engineering strategies may offer promising pathways forward. To suppress vibrational excitation losses, electron-impact processes could be tailored by increasing the reduced electric field (E/N), thereby shifting the electron energy distribution toward higher-energy channels such as electronic excitation and dissociation. This would present a paradigm shift in warm plasma-based gas conversion, where typically the vibrationally induced dissociation pathway is targeted (which is realized at lower E/N [17]), although in recent years, there is more and more consensus that this pathway is not feasible in warm plasmas (due to efficient vibrational-translational relaxation, as mentioned above [48,179–181]). Furthermore, nanosecond-pulsed plasmas could enhance energy-coupling efficiency and mitigate vibrational losses by depositing plasma power within a time window that precedes substantial thermal recombination of dissociation products. Under high-power operation, it is also feasible to establish high radical concentrations in the 10–30% range [70].

Another promising—and in our view, the most practical to realize—route is the incorporation of heat recovery. This is supported by the slight discrepancy between our OD model results and experimentally reported EC values by Fedirchuk et al. [152], where a minimum EC of $146 \text{ kJ.mol}^{-1}\text{-NH}_3$ and typical values around $200 \text{ kJ.mol}^{-1}\text{-NH}_3$ were

observed. The difference arises primarily from the OD model's inability to capture multidimensional effects such as heat transfer and turbulent mixing. In real systems, not all NH_3 feed passes through the central hot plasma column; some gas flows through cooler peripheral zones. Yet, NH_3 cracking still proceeds in these regions due to mixing, which redistributes heat and reactive species. These effects will be explored in more detail in Chapter 5.

For example, in our lowest-EC simulation case ($P_d = 1.55 \times 10^8 \text{ W.m}^{-3}$ in Figure 4-8), T_g reaches 2600 K at 10 ms. In a real (multidimensional) reactor, heat conduction would transfer some of this energy outward, preheating the incoming NH_3 and reducing the energy required to reach thermally active temperatures (above around 2000 K; see Figure 4-3b). Moreover, experimental reactor designs often separate the power deposition zone from the NH_3 inlet [152,156]. The hot plasma core—rich in N_2 , H_2 , and H atoms—absorbs most of the input energy and serves as a thermal source for heating the surrounding feed gas, see Chapter 3. Additionally, under these conditions, approximately 1–1.5% of the molar composition consists of H atoms (see Figure 4-5b above), which can diffuse outward, assist in NH_3 decomposition, or recombine, releasing heat—further enhancing energy efficiency. These multidimensional effects will be demonstrated in fully coupled CFD simulations in Chapter 5, highlighting the critical role of reactor design in heat recovery.

While the above describes natural “heat recovery” in real (multidimensional) reactors, we believe further improvements are possible by external heat recovery, where the hot effluent gas is recycled to preheat the inlet gas, so that a higher level of conversion is reached at the same plasma power, thus reducing the EC [14]. We plan to study this experimentally in our future work.

Finally, the strategic integration of plasma with complementary technologies—such as membrane reactors, post-plasma catalytic systems, or pre-plasma catalytic reactors (also called “reversed plasma catalysis” [192]) which also implicitly include heat recovery—should continue to be actively pursued. Such hybrid approaches could further enhance overall energy efficiency and broaden the applicability of plasma-assisted NH_3 conversion, particularly in centralized NH_3 cracking facilities, where large volumes of feedstock are processed, and high conversion is required.

4.4 Conclusion

We developed a new, extensive plasma chemical kinetics model, applicable in a wide range of electron temperature (T_e), gas temperature (T_g), and residence time (t_{res}), to investigate major performance characteristics of warm plasma NH₃ cracking—specifically NH₃ conversion and corresponding EC, product composition, and the time required to reach full conversion—and how they can be explained based on the underlying chemical mechanisms. Based on our modeling insights, we ultimately explore optimization strategies for the most cost-effective process.

The key findings of our study are as follows:

First, NH₃ conversion: Above a certain threshold temperature, the NH₃ conversion increases linearly with both T_e and T_g , but the slope decreases above a certain T_g before reaching full conversion. Full conversion occurs at $T_g = 2300$ K for $t_{res} = 10$ ms under pure thermal cracking, and plasma cracking enables full conversion for all T_g conditions at $T_e > 2.75$ eV. The onset and full conversion points in T_e and T_g vary depending on t_{res} , but the onset T_e and full conversion T_g become independent of t_{res} once it exceeds 1 ms. This is attributed to the strong significance of electron-impact dissociations and H-abstraction reactions of NH₃, respectively.

Second, final products: The final product composition is primarily governed by thermal equilibrium, which shifts with T_g but exhibits negligible dependence on T_e , except for increased concentrations of N and H atoms.

Third, time to reach full NH₃ conversion: The required time to reach full NH₃ conversion is dramatically reduced with increasing T_e , e.g., at 1100 K, it drops from thousands of years to the millisecond range. However, this difference gradually diminishes at higher T_g , and disappears as the thermal reaction kinetics become comparable to electron-induced reaction kinetics at T_g above 2700 K.

Fourth, underlying chemistry: The underlying chemical mechanism is the key factor for the above three characteristics. Notably, among 17 major reaction pathways, electron-impact NH₃ dissociation and H-abstractions with NH₃ are key for determining the observed trends.

Building on these insights, we further assessed the process energy efficiency, using EC as the key metric. For typical warm plasma operation under continuous power input, the minimum EC is 197 kJ.mol⁻¹-NH₃ at $T_g = 2500$ K. Attempts to reduce this limit—such as

avoiding post-conversion overheating or adding extra H radicals (motivated by their key role in promoting NH_3 dissociation via reaction R4)—were unsuccessful. Nevertheless, we identified significant energy losses (19% at 1500 K) via vibrational excitation, thus suggesting that shifting N_2 excitation toward electronic channels by increasing E/N at $T_g \approx 1500$ K could further improve efficiency.

Note that experimental studies have reported somewhat lower EC values, and this is likely due to heat transfer and turbulent mixing effects (i.e., “natural heat recovery”) that are not captured in our OD simulations. Therefore, other work should focus on more dimensional modeling to capture these effects. This will be explored in detail in Chapter 5. In addition, detailed experimental validation of our model remains essential. We therefore recommend measurements of H-radical densities and NH_2 and NH radicals using TALIF and LIF methods, respectively, as well as electron-density determination via Stark broadening of the $\text{H}\alpha$ emission line.

Overall, our work sheds important light on the benefits of plasma-based NH_3 cracking. Indeed, warm plasma reactions expand the effective operating conditions towards lower gas temperatures than pure thermal cracking, although at typical warm plasma conditions, the NH_3 cracking mainly proceeds by thermal reactions. Importantly, plasma reactions enable faster NH_3 conversion kinetics at gas temperatures below 2700 K.

Our model predicts a feasible reduction in EC to $157 \text{ kJ.mol}^{-1}\text{-NH}_3$, compared to $197 \text{ kJ.mol}^{-1}\text{-NH}_3$ which is typically observed for warm plasmas operated under continuous power supply, when employing plasma-initiated thermal cracking driven by nanosecond pulse plasma. We believe these findings are important for future research, as they underscore the urgent need for targeted engineering studies to experimentally realize and optimize such conditions. Furthermore, we believe that incorporating heat recovery could be another very promising strategy to further decrease the overall process energy cost.

Chapter 5

Multidimensional modeling of NH_3 cracking to understand turbulent effects

The content of this chapter is in part based on:

Effect of turbulent transport on plasma-based NH_3 cracking into H_2 : Insights from a RANS computational fluid dynamics model.

Maerivoet S., Quiroz Marnef R., Tsonev I., Reniers F., Bogaerts A.

Energy Conversion and Management, 2026, 364, 121741

<https://doi.org/10.1016/j.enconman.2026.121741>

and

Spatially resolved modelling of NH_3 cracking in warm plasma

Quiroz Marnef R.*, **Maerivoet S.***, Tsonev I., Reniers F., Bogaerts A.

Chemical Engineering Journal, 2025, 508, 161180

<https://doi.org/10.1016/j.cej.2025.161180>

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This chapter further explores plasma-based NH₃ cracking into H₂, and specifically the effect of turbulence, in a warm plasma, using a fully coupled 2D axisymmetric model solving gas flow dynamics and heating, chemical kinetics, transport of species, and current conservation. The model reaches good agreement with experiments over a wide range of flow rates and currents. In contrast to other warm plasma-based gas conversion chemistries, like CO₂ splitting and NO_x formation, increased turbulence appears detrimental to NH₃ cracking. It suppresses a hot afterglow, needed for additional “free” NH₃ conversion. Based on our model insights, we believe that further performance improvement is possible by extending the hot afterglow as much as possible, i.e., by avoiding turbulence or gas cooling, e.g., by keeping the afterglow chamber radius similar to that of the plasma reactor.

5.1 Introduction

In the previous chapter, we performed calculations over a wide range of operating conditions for plasma-based NH_3 cracking, both non-thermal and warm. We demonstrated that warm (or quasi-thermal, with gas temperature above 2000 K) plasma reactors are the most promising for NH_3 cracking. As mentioned in the previous chapter, Fedirchuk et al. [152] reported EC down to $146 \text{ kJ.mol}^{-1}_{\text{NH}_3}$, with room for improvement, e.g., in terms of the NH_3 fraction actively treated by the warm plasma.

Indeed, improvements are expected from better insights into the underlying mechanisms, which can be obtained from modeling. In previous chapter, the plasma model focused on chemical kinetics (by global models, not accounting for spatial effects or transport). Other researchers apply multidimensional CFD modeling [79–81,193], but typically account for only very limited chemistry, while describing transport of mass and energy.

In recent years, however, our group PLASMANT made significant efforts to integrate more chemistry into multidimensional plasma CFD models, specifically for warm plasmas (a few 1000s of K in gas temperature), where the chemistry is mainly thermal [194,195]. In Chapter 3, we developed a 2D warm plasma model for DRM with O_2 addition, to explore the thermal kinetics and to understand the energy balances. However, much more information can be obtained from such multidimensional coupled models, such as the flow dynamics, which would be interesting information for NH_3 cracking.

In this chapter, we present an improved version of the CFD model of Chapter 3, by incorporating the current conservation equations instead of assuming a certain heat source, and we apply this model to NH_3 cracking in a gliding arc plasmatron (GAP). Specifically, we study the effects of turbulent flow on plasma behavior and NH_3 cracking performance. Indeed, Van Poyer et al. [194] recently reported higher conversion in turbulent flow than in laminar flow in a CO_2 microwave plasma. The same mechanism is found for NO_x production from warm air plasmas [105]. However, we demonstrate here that the same benefits do not extend to NH_3 cracking, and we explain the underlying reasons for this different behavior. Based on these novel insights, we also propose measures to improve the performance of plasma-based NH_3 cracking.

5.2 Computational details

Our model is developed in 2D axisymmetric geometry but is combined with 3D and 0D modeling inputs, as described in Chapter 2. In short, we first solve the 3D gas fluid

dynamics equations without heating or reaction kinetics. This 3D flow field is used as input in our axisymmetric 2D model. The 2D model then solves the heat balance, chemical kinetics, species transport, and also (new in this chapter) the current conservation equations. This fully coupled model yields a very comprehensive insight into the NH₃ cracking mechanisms in the GAP, as explained in more detail below.

As stated in Chapter 2, while solving a fully coupled 3D model would yield the most physically accurate results by removing all axisymmetric approximations, this is currently infeasible due to the high computational cost of resolving the 3D mesh and fully coupling all physics with extensive chemistry sets. However, in future work, we would like to extend our model to 3D once higher computational capacity is available.

Furthermore, our model describes only thermal kinetics, and not plasma kinetics. This approximation is necessary because a 2D CFD model that includes plasma kinetics, coupled with other complex physics (such as highly swirling gas flows and heat balance), is still computationally too expensive. We believe, however, that this approximation of thermal chemistry is valid at the conditions under study, based on our modeling work of warm NH₃ plasmas in Chapter 4. This modeling shows that most of the energy in warm plasma is indeed dissipated as heat, and that this heat converts NH₃ into N₂ and H₂. The model indeed revealed that nearly all dissociation occurs via thermal pathways, and that electrons serve only as an efficient gas heater, rather than as a chemical pathway inducer (see Chapter 4). Furthermore, previous CFD models developed within our group PLASMANT, assuming only thermal chemistry, are in good agreement with experimental data, not only for NH₃ cracking (see this chapter) but also for CO₂ conversion [194–196] and air plasmas [197]. When computational resources allow in the future, however, we do plan to include the plasma kinetics in our models to further improve their accuracy and applicability to other plasma systems.

5.2.1 Reactor schematic

Figure 5-1 depicts a schematic representation of the GAP studied in this work. One main inlet is split into six tangential inlets, which are modeled in the 3D geometry. The top of the reactor consists of a high-voltage electrode (light blue) separated from the grounded electrode (green) by electrical insulation (yellow). The arc plasma is created at the top of the high-voltage electrode and propagates downward into the afterglow gas chamber, where it attaches to the grounded electrode. The GAP is characterized by strong forward and reverse (downward) vortex flows, which ensure that the arc starts at the top of the high-voltage electrode and does not attach to the grounded electrode before entering

the afterglow gas chamber [153,198]. This is experimentally observed through damage on the bottom side of the grounded electrode and through camera images [199]. As the plasma is contained by a vortex flow, the attachment point at the grounded electrode rotates with it, similar to the rotating attachment observed by Lee et al. [62].

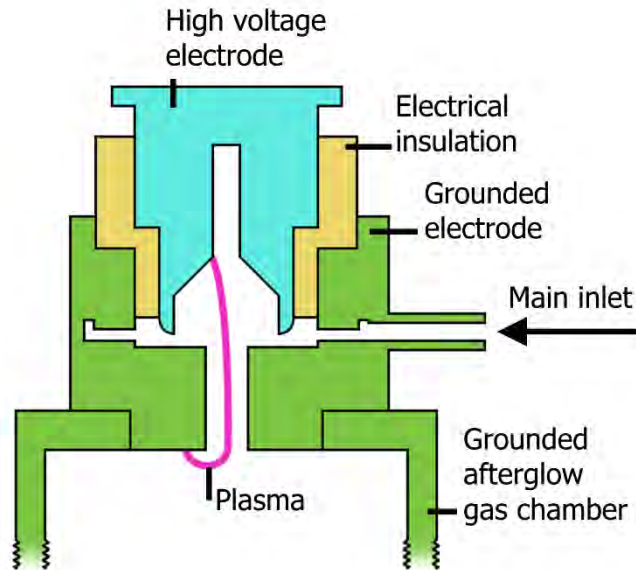


Figure 5-1 - Schematic representation of the gliding arc plasmatron (GAP). The high voltage electrode is indicated in light blue, the electrical insulation in yellow, and all grounded parts are indicated in green. A schematic representation of the plasma is indicated in purple. Dimensions are indicated in Figure 5-2 below. The afterglow gas chamber extends to 80 mm.

To simplify the model, the top open volume of the GAP is assumed closed, as this does not affect the flow dynamics or the location of the arc, because we model this in a 2D system, and it has to be centered anyway.

Furthermore, although in reality the arc is attached to the upper edge of the afterglow chamber, i.e., the grounded electrode (anode, cf. Figure 5-1 and see text above), this would cause the plasma arc to be off-center in our 2D model, resulting in a dented umbrella-shaped plasma in 3D, which is incorrect and would severely affect the flow dynamics. Therefore, we defined a virtual ground at the entrance of the afterglow gas chamber in our 2D model (see Figure 5-3), to ensure that the plasma arc is centered at the symmetry axis.

5.2.2 Geometry and boundaries

As mentioned above, we developed a 3D gas fluid dynamics model without heating or reaction kinetics to provide the 3D flow field as input for the 2D model. The 3D model results are presented in section 5.3.4 below, including the model geometry and 3D mesh. The 3D model only solves the RANS equations following the description in Chapter 2. Currently, Large Eddy Simulations and Reynolds Stress Models, combined with the fully coupled physics and chemistry in our 2D model, are too computationally expensive. Indeed, we must fully couple the chemical kinetics and heat balance to realistically describe the NH₃ cracking mechanisms. Therefore, we applied the RANS SST formulation, as it is reported to be the most accurate set of equations in capturing swirling flow behavior at reasonable computational costs [200]. Furthermore, recent modeling studies within our group PLASMANT have explored differences between laminar and SST RANS formulation for warm plasmas operating in air (for NO_x production) and for CO₂ conversion, finding slightly better agreement with experiments when applying the SST formulation [195–197]. All models are solved using COMSOL Multiphysics® [108].

The boundary conditions for the 3D flow model can be found in Table 5-1 for the velocity field (u), pressure (p), turbulent kinetic energy (ϵ), and turbulent dissipation rate (ω). The exact boundaries and dimensions can be found in Figure 5-2.

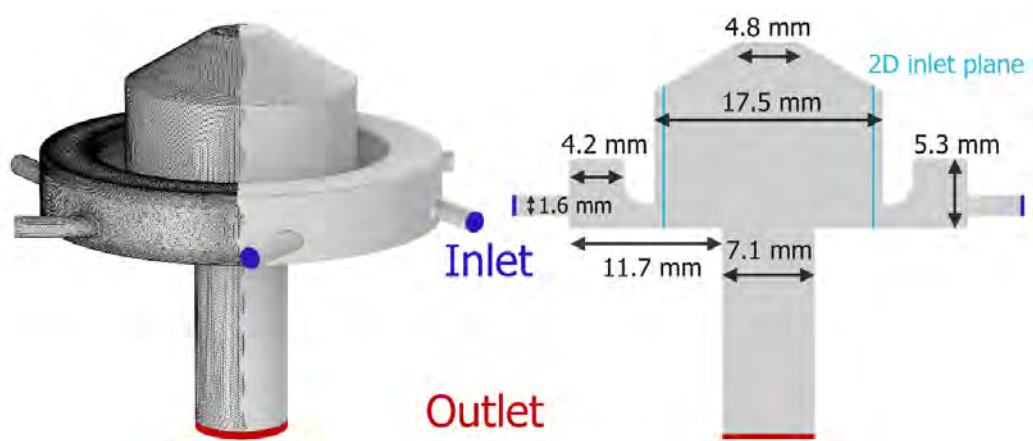


Figure 5-2 - 3D depiction of the gliding arc plasmatron (GAP) reactor with a visual representation of the mesh size (left) and dimensions of the 3D model shown in a 2D cut plane (right). The gas inlet and outlet are represented in dark blue and red, respectively. The wall is grey. The inlet plane for the 2D model is shown in light blue in the right figure.

Table 5-1 - Boundary conditions of the fluid flow variables in the 3D model [110].

	p (Pa)	u (m s⁻¹)	ε (m² s⁻²)	ω (s⁻¹)
<i>Inlet</i>	/	$-\int_{\partial\Omega_{in}} \mathbf{u} \cdot \mathbf{n} dS$ $= V_0$	$\varepsilon = 0$ $\nabla \varepsilon \cdot \mathbf{n} = 0$	$\omega_w = \frac{6\mu}{\rho\beta_1 l_{ref}^2 \epsilon_m}$ $\nabla \omega \cdot \mathbf{n} = 0$
<i>Walls</i>	/	$\mathbf{u} = \mathbf{0}$	$\nabla \varepsilon \cdot \mathbf{n} = 0$	$\omega_w = \frac{6\mu}{\rho\beta_1 l_{ref}^2 \epsilon_m}$
<i>Outlet</i>	$[-p\mathbf{I} + \mathbf{K}]\mathbf{n}$ $= -p_0\mathbf{n}$ $p_0 = 0$	/	$\nabla \varepsilon \cdot \mathbf{n} = 0$	$\omega_w = \frac{6\mu}{\rho\beta_1 l_{ref}^2 \epsilon_m}$ $\nabla \omega \cdot \mathbf{n} = 0$

The boundary conditions (and accompanying equations) correspond to fully developed flow at all six inlets, with a total flow rate of 10 to 20 SLM at 293.15 K. The walls are treated based on a no-slip wall condition with low Reynolds wall treatment, yielding the shown equation for ω_w , i.e., the turbulent dissipation at the wall. Finally, the outlet is treated by setting the pressure, p_0 , to 0 atm. This is in addition to a reference pressure of 1 atm in the full reactor. Furthermore, backflow is not suppressed at the outlet.

In Table 5-1, $\mathbf{u}$ is the velocity field, $\partial\Omega_{in}$ is the inlet boundary, S is the inlet surface, V_0 is the inflow flow rate, p_0 is the outlet pressure, $\mathbf{K}$ is the viscous stress tensor, μ is the dynamic viscosity, ρ is the gas density, β_1 is the 0.075, l_{ref}^2 is the reference length based on geometry and ϵ_m is machine epsilon.

Figure 5-3 provides a 2D representation of how the GAP is modeled in the 2D framework, with all important boundary conditions (right) and dimensions (left) indicated. The plasma arc is centered at the symmetry axis by defining a virtual ground at the entrance of the afterglow gas chamber (see above); the latter is 80 mm long, and thus not shown to scale.

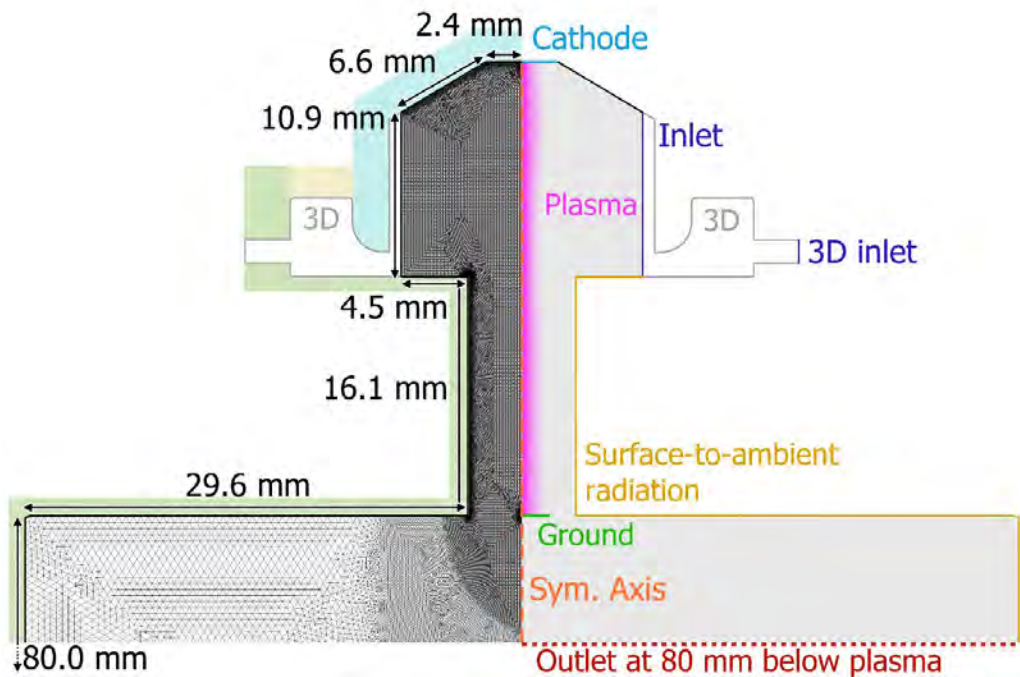


Figure 5-3 - 2D axisymmetric model geometry, mirrored around the symmetry axis, showing the mesh and dimensions on the left side, and boundary conditions on the right side. The central plasma arc is presented in purple. The symmetry axis is shown in orange, the cathode (top, maintaining a set current) is in light blue, the electrical ground (anode) is in green, the inlet plane is in dark blue, boundaries where surface-to-ambient radiation is applicable are indicated in yellow, and the outlet of the afterglow is at 80 mm. The actual 3D geometry is added in grey. Border colors on the left-hand side correspond to the schematic of Figure 5-1.

As the 2D model uses cylindrical coordinates, the 3D flow velocities in Cartesian coordinates are transformed to flow velocities in cylindrical coordinates, as explained in Chapter 2.

The boundary conditions for the 2D model can be found in Table 5-2 (for fluid flow, i.e., velocity field (u), pressure (p), turbulent kinetic energy (ϵ), turbulent dissipation rate (ω)) and in Table 5-3 (for all other variables: temperature (T), conductive heat flux (q), mass fractions of all species (w_i), molar flux (J_i) and voltage (V)) [110,113,120,121]. The specific boundaries are shown in Figure 5-4, which is a simplified schematic of the plasma reactor.

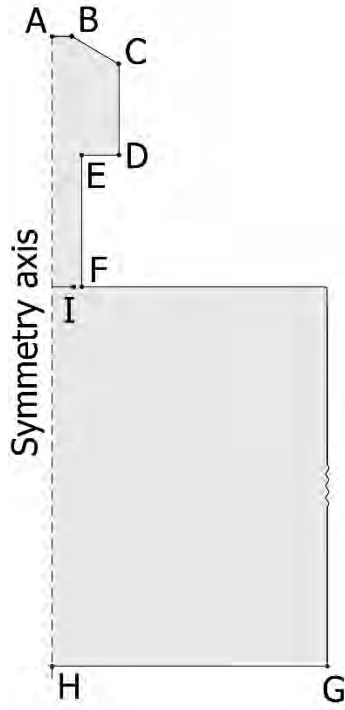


Figure 5-4 - Simplified schematic of the GAP plasma reactor, to indicate the boundaries (AB: Cathode, CD: inlet, GH: outlet, II': Ground, BC-DG: wall with radiation loss). The serrated line between points F and G indicates a compression of this distance.

Table 5-2 - Boundary conditions of the fluid flow variables in the 2D model [110].

	p (Pa)	u (m s ⁻¹)	ε (m ⁻² s ⁻²)	ω (s ⁻¹)
<i>Inlet</i>	/	$u = u_0$	$\varepsilon = \varepsilon_0$	$\omega = \omega_0$
CD				
<i>Walls</i>	/	$u = 0$	$\nabla \varepsilon \cdot \mathbf{n} = 0$	$\omega = \frac{6\mu}{\rho\beta_1 l_{ref}^2 \epsilon_m}$
AC & DG				
<i>Outlet</i>	$[-p\mathbf{I} + \mathbf{K}]\mathbf{n} = -p_0\mathbf{n}$	/	$\nabla \varepsilon \cdot \mathbf{n} = 0$	$\nabla \omega \cdot \mathbf{n} = 0$
GH	$p_0 = 0$			$\omega = \frac{6\mu}{\rho\beta_1 l_{ref}^2 \epsilon_m}$

The walls and outlet in the 2D model are treated the same way as in the 3D model. This means no-slip, low-Reynolds-number wall treatment, and backflow is not suppressed, with an outlet pressure set to 0 Pa. The inlet is treated differently, with the 3D flow field and turbulence variables mapped onto the 2D model using the equations in Chapter 2.

In Table 5-2, $\mathbf{u}$ is the velocity field, $\mathbf{u}_0$ is the imposed velocity field, ε_0 is the imposed turbulent kinetic energy, ω_0 is the imposed turbulent dissipation rate, p_0 is the outlet pressure, $\mathbf{K}$ is the viscous stress tensor, μ is the dynamic viscosity, ρ is the gas density, β_1 is the 0.075, l_{ref}^2 is the reference length based on geometry and ε_m is machine epsilon.

Table 5-3 - Boundary conditions of the non-fluid flow variables in the 2D model [113,120,121].

	T (K)	$\mathbf{q}$ (W m ⁻²)	$\mathbf{w}_i$ (-)	$\mathbf{J}_i$ (mol m ⁻² s ⁻¹)	Electric
<i>Cathode</i> AB	/	$-\mathbf{n} \cdot \mathbf{q} = 0$	/	$-\mathbf{n} \cdot \mathbf{j}_i = 0$	$\int \mathbf{J} \cdot \mathbf{n} dS = I_0$
<i>Electric insulation</i> BC	/	$-\mathbf{n} \cdot \mathbf{q} = 0$	/	$-\mathbf{n} \cdot \mathbf{j}_i = 0$	$\mathbf{J} \cdot \mathbf{n} = 0$
<i>Inlet</i> CD	T = 293.15 K	/	$w_i = w_{0,i}$	/	$\mathbf{J} \cdot \mathbf{n} = 0$
<i>Walls</i> DG	/	$-\mathbf{n} \cdot \mathbf{q} = s_e \sigma (T_{amb}^4 - T^4)$	/	$-\mathbf{n} \cdot \mathbf{j}_i = 0$	$\mathbf{J} \cdot \mathbf{n} = 0$
<i>Outlet</i> GH	/	$-\mathbf{n} \cdot \mathbf{q} = 0$	$-\mathbf{n} \cdot \rho D_i^m \nabla w_i = 0$	/	$\mathbf{J} \cdot \mathbf{n} = 0$
<i>Ground</i> II* I* = axial-mirrored I	/	/	/	/	V = 0

The heat transfer boundary conditions are as follows: the gas inlet is set to 293.15 K, while all inner walls and the gas outlet are treated as having no conductive heat flux. The outer wall is subject to radiative emission with an emission coefficient of 0.75 and an outer temperature of 293.15 K. No convective heat transfer at the outer wall and no additional conductive heat transfer are applied. No other cooling mechanisms are present in the model.

The boundary conditions for transport of species are treated as follows: the gas inlet consists of 100 % NH₃, there is no flux of any kind through any wall, there is no molecular diffusion through the outlet, and all species leave the system at the outlet via convection.

The current conservation boundary conditions are treated as follows: Current is imposed at the top boundary (AB), and a ground is defined at (II*) by setting the voltage to 0 V. All other boundaries are considered electrically insulated. This enables the model to calculate an electric field, ensuring that current is conserved from the top boundary to the ground.

In Table 5-3, ΔH is the sensible enthalpy, T_{amb} is ambient (room) temperature, s_e is the surface emissivity set at 0.75, σ is the Stefan-Boltzmann constant, $w_{0,i}$ is the initial weight fraction, being 1 for NH₃ and 0 for all other species, ρ is the gas density, D_i^m is the molecular diffusion coefficient, and I_0 is the user-defined total current flowing through the cathode.

5.2.3 Turbulent transport modifier

Understanding turbulent transport effects is achieved by applying a turbulent transport modifier to the heat transfer and species transport equations.

The temperature is governed by the heat transfer equation [120,121]:

$$\rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot (-(k + Fk_T) \nabla T) + \sum_i \bar{H}_i r_i + \sum_i \mathbf{j}_i \cdot \nabla \bar{H}_i = \mathbf{E} \cdot \mathbf{J} \quad [86]$$

This equation is almost exactly equivalent to the heat transfer equation in Chapter 2. The second term introduces the turbulent transport modifier.

F is the user-introduced unitless turbulent transport modifier. The aim of our work is to provide a sensitivity analysis of the effects of turbulence by artificially increasing and decreasing this factor, F . Note that this factor is inversely proportional to the turbulent Prandtl number. The Prandtl number in our study is approximated using the Kays-

Crawford formulation [201]. For example, a higher turbulence by a factor of $\times 2$ means that all equations are solved again with the same input parameters, except for F , which is 2. This corresponds to dividing the turbulent Prandtl number by a factor 2. In the standard case, describing the real system, F is equal to 1. We decided to introduce the unitless turbulent transport modifier to directly control the changing turbulence effects. Indeed, isolating the turbulence effect in this manner and resolving the full system of equations allows us to gain better insight into the underlying processes and effects.

The weight fractions of species are governed by the transport of species equation [121]:

$$\nabla \cdot \mathbf{j}_i + \rho(\mathbf{u} \cdot \nabla)w_i = r_i \quad [87]$$

Here w_i represents the weight fraction of species i . The diffusive flux vector is calculated from the Maxwell-Stefan diffusion model as follows [121]:

$$\mathbf{j}_i = - \left(\rho D_i^m \nabla w_i + \rho w_i D_i^m \frac{\nabla M_n}{M_n} + \rho w_i F D_{T,i} \nabla w_i - \mathbf{j}_{c,i} \right) \quad [88]$$

The turbulent transport modifier is repeated here; the treatment of the turbulent diffusivity follows that of the turbulent Schmidt number, based on the Kays-Crawford formulation, as for the turbulent thermal conductivity. Varying the turbulent transport modifier affects both the heat transfer equation (equation 86) and the transport equation of species (equation 88).

5.2.4 Chemistry set

The right-hand side of equation 87 represents the net production rate of each species i , defined by the sum of all production reactions minus all loss reactions. The complete reaction set for all species included in the model is presented in the Supporting Information of our paper [202]. We do show the result of the reduction process in section 5.3.1. The species considered in our model are listed in Table 5-4. We do not include electrons, ions, or excited states in our model, nor do we solve an electron energy balance equation. Therefore, we cannot draw any conclusion on electron density, emission spectra, or the plasma sheet near the electrodes. We compare our calculated conversion and EC with experiments, where we achieve good agreement, since conversion is mainly thermally driven, as also demonstrated in Chapter 4 [171]. Solving the electron energy balance may result in a somewhat higher conductivity in the plasma core, which could yield a somewhat lower core plasma temperature. However, this effect is negligible in the thermal chemistry, as the plasma core always exhibits local chemical equilibrium due to extremely fast thermalization; see Chapter 4.

Table 5-4 - Species included in the model

H	NH	trans-N ₂ H ₂ (t-N ₂ H ₂)
H ₂	NH ₂	cis-N ₂ H ₂ (c-N ₂ H ₂)
N	NH ₃	H ₂ NN
N ₂		N ₂ H ₃
		N ₂ H ₄

5.2.5 Performance metrics

The NH₃ conversion in the model is calculated by the ratio of the molar flow rate of NH₃ at the outlet compared to the total molar inflow rate of NH₃, which can be written as follows:

$$\chi_{model} = \frac{\dot{n}_{NH_3}^{in} - \dot{n}_{NH_3}^{out}}{\dot{n}_{NH_3}^{in}} \quad [89]$$

Here, $\dot{n}_{NH_3}^{in}$ is the molar inflow rate of NH₃ and $\dot{n}_{NH_3}^{out}$ is the molar outflow rate of NH₃. Computationally, the molar flow rates are calculated by integrating over the inlet or outlet surface.

$$\dot{n}_{NH_3}^{in/out} = \int_{A \text{ in/out}} u_n c_{NH_3} dA \quad [90]$$

Here A is the area of either the in or outlet, u_n is the velocity normal to the surface and c_{NH_3} is the molar concentration of NH₃.

The experimental conversion is calculated using equation 91 as introduced by Fedirchuk et al. for undiluted NH₃ [152]:

$$\chi_{exp} = \frac{1 - y_{NH_3}^{out}}{1 + y_{NH_3}^{in}} \quad [91]$$

Here, $y_{NH_3}^{out}$ is the fraction of NH₃ at the outlet, determined using a thermal conductivity detector by measuring H₂, and $y_{NH_3}^{in}$ is the fraction of NH₃ at the inlet, here equal to 1. Only N₂ and H₂ were observed as products in the experiments; scans for additional products like N₂H₄ were performed, but only a negligible amount was found (see details in the work of Fedirchuk et al. [152]). Furthermore, the NH₃ used in the experiments is 99.96 % pure anhydrous NH₃ from Air Liquide, and no significant overpressure was

measured at the outlet. The above equation automatically accounts for dilution or gas expansion, which is crucial for accurate measurements [140]. Details on the measurement methods for the outlet composition, including the dry basis of the system and the excess NH₃ at the outlet, can be found in Fedirchuk et al. [152].

The EC is evaluated as the ratio of the SEI to the conversion. The SEI, in turn, is the ratio of the total input power (P) to the total input molar flow rate. Combined, the equation for EC for both the experiments and the model is as follows:

$$EC = \frac{P}{\chi \cdot \dot{n}_{NH_3}^{in}} \quad [92]$$

The experimental power is taken from the work of Fedirchuk et al. [152]. The modeled power deposition is obtained from the volume integral of the Joule heating power density, following equation 93:

$$P_{model} = \int_V Q_h dV \quad [93]$$

Here, Q_h is the electromagnetic volumetric loss density from the current conservation equations, and V is the total modeled volume

Throughout this work, the EC represents the energy required by the current system to crack 1 mole of NH₃. The formation EC of H₂ is thus multiplied by 1.5, due to 1.5 moles of H₂ being formed per mole of NH₃ destroyed.

5.3 Results and discussion

In the next sections, we first present the chemical reduction of the NH₃ thermal set. Afterward, we present experimental validation of our model, followed by a pathway analysis and our 3D flow model results. Subsequently, we present detailed results from our 2D model to better understand the NH₃ cracking mechanisms in the GAP and, specifically, to answer our research question on how turbulent flow affects plasma behavior and NH₃ cracking performance. Finally, we give suggestions for improved reactor designs, based on our modeling insights.

5.3.1 Chemical reduction results

The full chemistry set, presented in Supporting Information of our paper [202], is reduced using the method described in Chapter 2. Both the reduced and full sets are available in the published paper [202]. Figure 5-5 compares the full and reduced kinetic

sets (solid and dashed lines, respectively) following the reduction method for pure NH_3 decomposition at 2800 K. As the maximum allowed tolerance is set at 0.1 % absolute deviation of any species from the total molar concentration, no significant difference can be observed in Figure 5-5a, which shows the molar concentrations on a linear scale. Figure 5-5b depicts the molar concentrations on a logarithmic scale, where differences are evident at very low concentrations. As any thermodynamic or transport variable depends on the molar concentration of the species, the large relative error observed for the species with low concentrations is negligible for the overall plasma behavior. This is the case as long as the individual properties of a species (enthalpy, entropy, ...) do not differ by orders of magnitude from all other species.

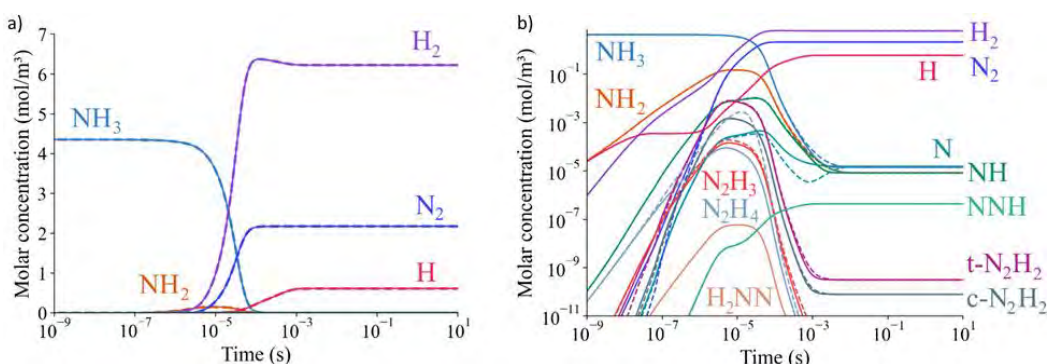


Figure 5-5 - Molar concentration of NH_3 and (major) decomposition products, as a function of time at 2800 K, in linear (a) and logarithmic (b) scale. Full lines represent the full kinetic set, while dashed lines represent the reduced kinetic set.

Due to its very fast kinetics, NNH is removed from the reduced set to avoid numerical instabilities. Figure 5-6 compares the full and reduced kinetic sets (solid and dashed lines, respectively), with NNH replaced by N_2 and H in the reduced set, again for pure NH_3 thermal cracking at 2800 K.

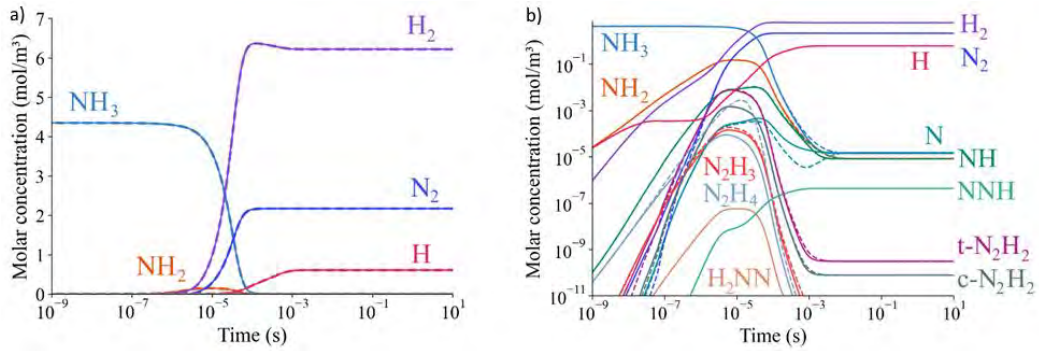


Figure 5-6 - Molar concentration of NH₃ and (major) decomposition products, as a function of time at 2800 K, in linear (a) and logarithmic (b) scale. Full lines represent the full kinetic set, while dashed lines represent the reduced kinetic set without NNH.

We can see that removing NNH from the reduced set has a negligible effect on the kinetics, even though NNH has a higher molar concentration than other intermediate species. This is because the destruction of NNH to N₂ and H is extremely fast, and any NNH formed is thus the result of the detailed balanced reverse rate. The major effect of the chemistry reduction (both with and without NNH in the model) seems to be an overestimation of the N₂H₄ concentration by an order of magnitude around 10 μs . This means we cannot use our reduced model to study N₂H₄ production in warm plasma, but that is not the purpose of this work. On the other hand, this overestimation has a negligible effect on the thermodynamic properties of the model, as the N₂H₄ molar concentration never exceeds $10^{-4} \text{ mol.m}^{-3}$.

5.3.2 Experimental validation of the model

Our model is validated in a wide range of SEI, for five different gas flow rates, ranging from 10 to 20 SLM. Figure 5-7 illustrates the conversion (left panels) and EC (right panels) for all flow rates, comparing the model results with the experimental data reported by Fedirchuk et al. [152]. The data shown in Figure 5-7 serves as a good first validation for our thermal modeling approach, although more validation in the future (e.g., on gas temperature, electron temperature, and density when they could be explicitly calculated, and species densities in the plasma) could provide further credibility of the model.

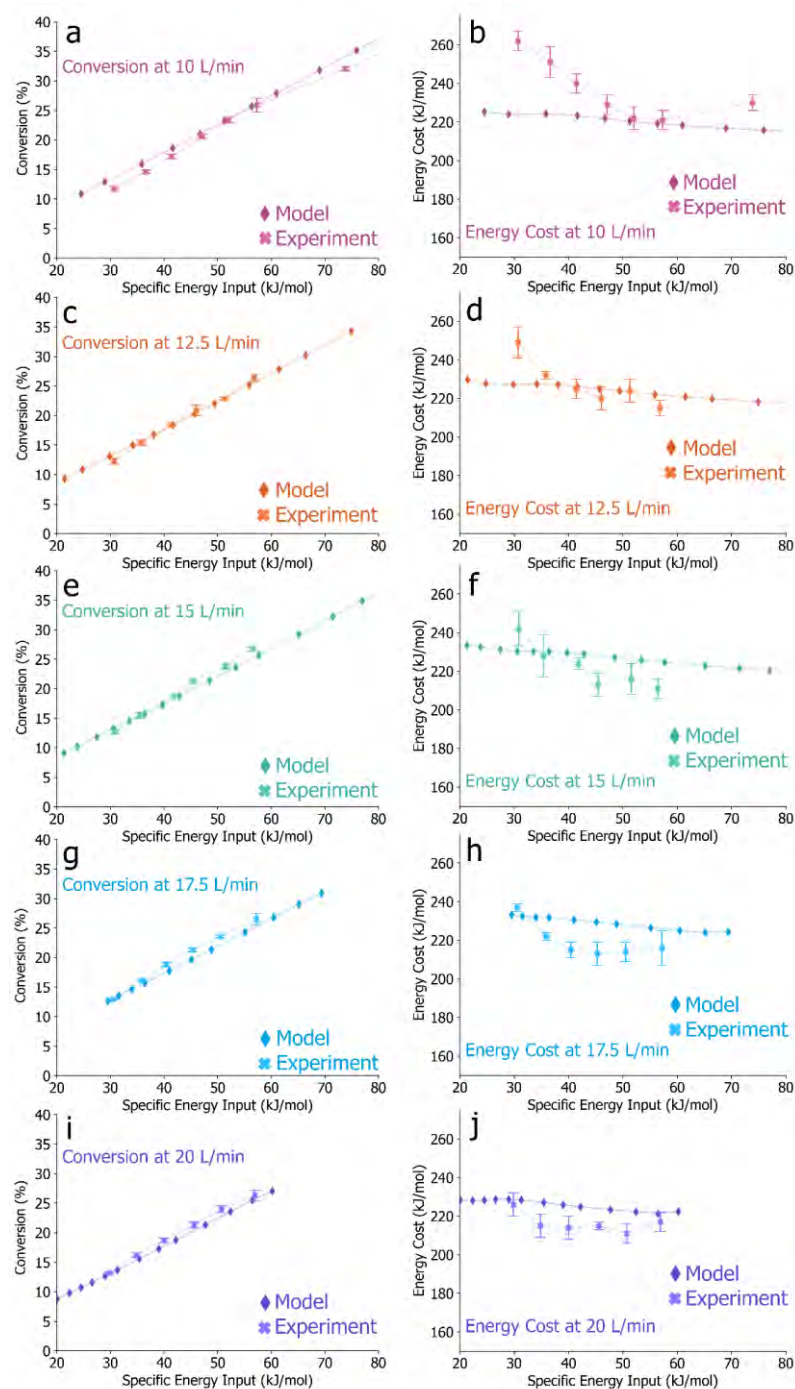


Figure 5-7 – Experimental [152] (x) vs modeled (◆) conversion (left) and energy cost (right), for 10 (a, b), 12.5 (c, d), 15 (e, f), 17.5 (g, h) and 20 (i, j) SLM NH₃ flow rate.

We observe very good agreement in the conversion across all flow rates, given that no fitting was used in our model. The linear trend observed in the experiments is accurately captured by our model. The EC also yields reasonable agreement with the experiment. Note that the experimental datapoints of EC have much larger error bars than the datapoints of conversion. This is because EC is the ratio of SEI to conversion, so the errors in both SEI and conversion propagate to much larger error bars for EC. While the model cannot reproduce the rise in EC with lower SEI (cf. the first data points in the right panels of Figure 5-7), it can reproduce EC for higher SEI values, and overall, the values are in the correct order of magnitude. We attribute the rise in EC (and the accompanying drop in conversion) at low SEI values to plasma instabilities that are not yet captured in our models. Detaching and reattaching the arc at unstable conditions will heat the afterglow to some extent. This can only be captured using 3D time-resolved simulations that include solving the plasma chemistry, which is beyond the scope of this work. However, note that the scale of the EC axis does not start at 0 kJ.mol⁻¹, but at 150 kJ.mol⁻¹, so the difference in experimental and modeled EC is still relatively small.

5.3.3 Reaction pathway analysis in a pin-to-pin arc plasma reactor

Before diving into the turbulent flow effect in the GAP reactor, we first need to detail the chemical kinetics. As mentioned in Chapter 4, thermal NH₃ decomposition occurs over a narrow temperature range (2400-3000 K) in the plasma. To understand which reactions are important at different positions, we need to perform a detailed pathway analysis. Figure 5-8 illustrates the pathway analysis for an SEI of 58 kJ.mol⁻¹ for a pin-to-pin arc plasma reactor. We do not present this pathway analysis for the GAP reactor, as there is no large afterglow for the pin-to-pin reactor, which makes it a somewhat easier system to analyze. However, the conclusions drawn here can be readily applied to the GAP reactor as well, and the plot is very similar to the pathway analysis presented in Chapter 3. The most important net reaction rates are shown. For the intermediate species (NH₂, NH, trans-N₂H₂, cis-N₂H₂), the branching ratios of the most important reactions (also to other species) are depicted next to the reaction arrows. Contributions < 1% are omitted for clarity. Any reaction denoting (+ M) requires a neutral third body as a collisional partner to proceed.

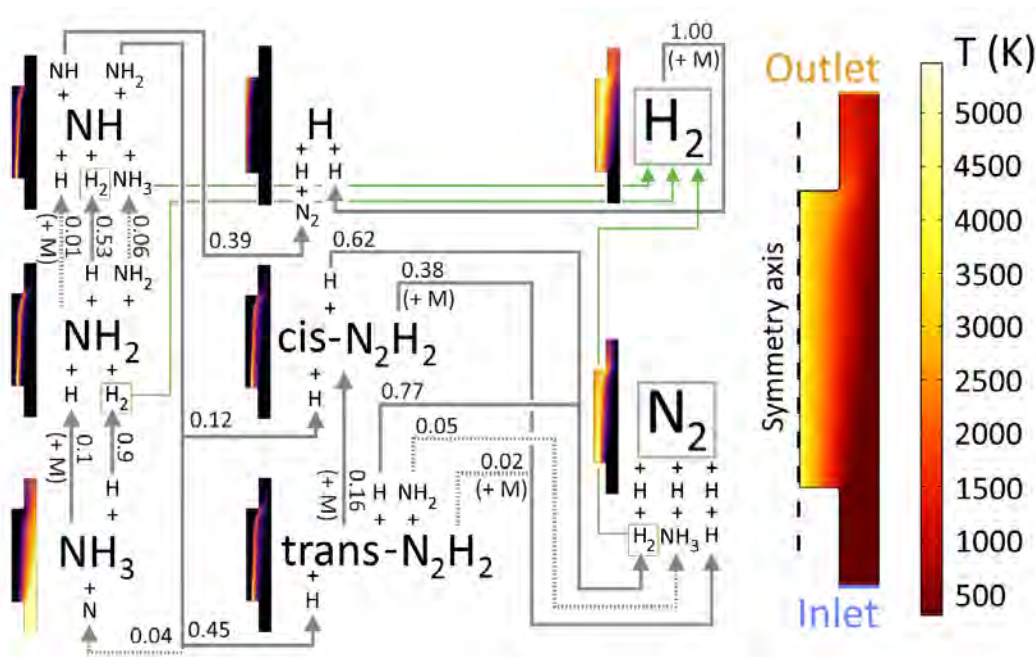


Figure 5-8 - Reaction pathway analysis of NH_3 decomposition at 5 NLM, SEI = 58 kJ/mol. The 2D plots illustrate the mole fractions of the species, while the temperature profile is shown on the right. The arrow directions correspond to the net rates of the reactions in the complete reactor. The branching ratios for the destruction of a species are denoted next to the arrows. (+ M) is shown if the reaction requires a third body as a neutral collision partner to proceed. Reactions contributing to less than 10 % of the species destruction are indicated with a dashed arrow, while reactions contributing less than 1 % are omitted, for clarity. Importantly, all produced (green) H_2 molecules are linked to the final H_2 product with green arrows.

The general trend of NH_3 decomposition is clearly shown in Figure 5-8: NH_3 decomposes into NH_2 , followed by NH , after which the pathway branches, as detailed below. Taking a more detailed look, NH_3 is broken down to NH_2 via two reactions: the reaction with H accounts for 90% of the NH_3 destruction (and leads to H_2 formation), but it is not possible without the reaction of NH_3 with M , which creates the first necessary H atoms. Therefore, the reaction of NH_3 with M is important to initiate the NH_3 decomposition.

Like NH_3 , the decomposition of NH_2 to NH mainly occurs via reaction with an H atom (contribution of 53% and leading to H_2 formation). Furthermore, the NH_2 radical can also react with itself to form NH and NH_3 , or it can decompose into NH upon collision with M (although both reactions are of minor importance), and in addition, NH_2 reacts with NH to form both N_2H_2 isomers (as well as new H atoms) or to form NH_3 and N . Because not all NH_2 reacts to NH , the sum of the branching ratios for NH_2 destruction to NH is not equal to one. If we include the reaction of NH and NH_2 to cis- and trans- N_2H_2 and the

reaction of NH₂ with trans-N₂H₂ into N₂, NH₃, and H, the sum of the branching ratios is equal to one.

From NH onwards, several pathways are possible. First, the reaction of NH with itself gives rise to the formation of N₂ and two H atoms (contribution of 39 %). In addition, NH reacts with NH₂, forming either trans-N₂H₂, cis-N₂H₂, or NH₃, as mentioned above. The first two pathways are much more significant, accounting for 45 % and 12 % of NH destruction, respectively. While trans- and cis-N₂H₂ follow similar reaction pathways for both production and destruction, the major difference between these species lies in their enthalpy. Indeed, cis- and trans-N₂H₂ have an enthalpy of formation of 212 vs 200 kJ.mol⁻¹ at 300 K, and 392 vs 380 kJ.mol⁻¹ at 2800 K. As such, starting from trans-N₂H₂, three reactions lead to N₂ formation, with the reaction of H as co-reactant being the most important (and again producing H₂). However, 16 % of trans-N₂H₂ is converted via isomerization to cis-N₂H₂, after which cis-N₂H₂ reacts with H or with M into N₂ and H/H₂. Therefore, while cis-N₂H₂ is an important intermediate from NH to N₂, it is also important in the trans-N₂H₂ destruction pathway.

It is important to note that the key reactions from NH₃ to NH₂ and NH produce H₂ as a co-product, with H used as a co-reactant. In addition, both major cis- and trans-N₂H₂ decomposition pathways to N₂ (upon reaction with H) also create H₂. Therefore, all these produced H₂ molecules are also highlighted in green in Figure 5-8, as they are the major reaction product, and they are linked to the final H₂ product with green arrows. Figure 5-8 also shows an arrow for the decomposition of H₂ towards H, which is dominant over H atom recombination into H₂.

The different intermediate species occur in different temperature ranges: both cis- and trans- N₂H₂ are formed between 2150 and 2600 K, and they are destroyed between 2600 K and 2900 K, while NH₂ is mainly formed between 2200 and 2700 K, NH is formed between 2500 and 2800 K, and the H atoms mainly reside in the plasma core at temperatures above 2700 K. All these reactions happen in a relatively narrow zone between 2 and 3.5 mm from the symmetry axis. Therefore, we call the zone with temperatures between 2400 and 3000 K the chemically active region, where most NH₃ is destroyed, and most products are formed. The high plasma temperature in the central column plays a significant role in providing the crucial H atoms to this zone, and it is thus not necessarily detrimental that the temperature is higher here than strictly needed. Indeed, as higher temperatures increase the number of H atoms, more H atoms can diffuse towards the chemically active region, further contributing to efficient NH₃

conversion. Furthermore, as we did not include charged species in our modeling and the plasma center is the current-carrying region within the reactor, we cannot draw firm conclusions about the plasma core chemistry. While we observe that H radicals are produced in the plasma core and diffuse outward, electron-impact chemistry will likely generate additional H radicals via H_2 dissociation. This process might influence the NH_3 conversion chemistry in the chemically active zone by increasing the outward flux of H radicals.

Validation of chemical species pathways is difficult but very important, as most of the time, only the resulting plasma composition is known. Spatial imaging of plasmas is therefore an important tool for multidimensional plasma modelers to validate or refute their models. As the conclusions from this section of the multidimensional model are the same as those drawn on high-temperature NH_3 cracking in Chapter 4, this would also partially validate the thermal NH_3 set.

5.3.4 3D modeling results

Now that we understand the chemical kinetics, we can come back to the flow profiles. Figure 5-9 presents a 3D plot of the streamlines at a gas flow rate of 20 SLM on the left-hand side (a), and a 2D cut plane of the y-z plane, including streamlines on the right-hand side (b), both showing the flow magnitude.

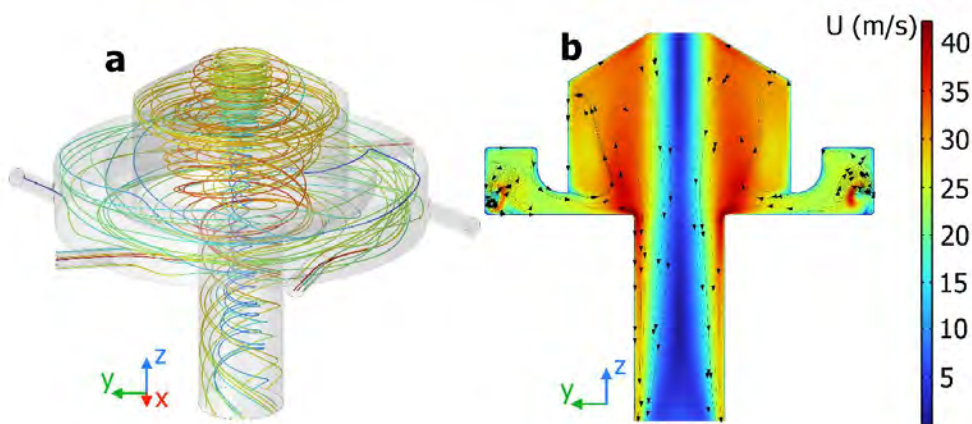


Figure 5-9 - 3D streamlines (a) and a 2D cut plane (b), including streamlines, both showing the velocity magnitude of the 3D gas flow simulation.

The streamlines in Figure 5-9a illustrate a strong vortex flow, initially flowing upward, after which a narrow vortex channel drags the flow downwards. Near the outlet, the central vortex is slower than the outer vortex. Figure 5-9b illustrates this more clearly:

the streamlines indicate that the gas in the center of the vortex passes close to the top of the reactor and flows more slowly, while the gas near the walls at the outlet flows faster. These results confirm the presence of a very strong vortex flow to stabilize the plasma.

The input at the inlet plane for the fully coupled 2D model (indicated in Figure 5-2 and Figure 5-3) is obtained by first solving the 3D gas flow model, and azimuthally averaging over a cylinder mantle at a radius of 8 mm. Figure 5-10a indicates this cylinder mantle over which the cylindrical velocities and turbulence parameters are averaged, over an angle θ from 0 to 2π .

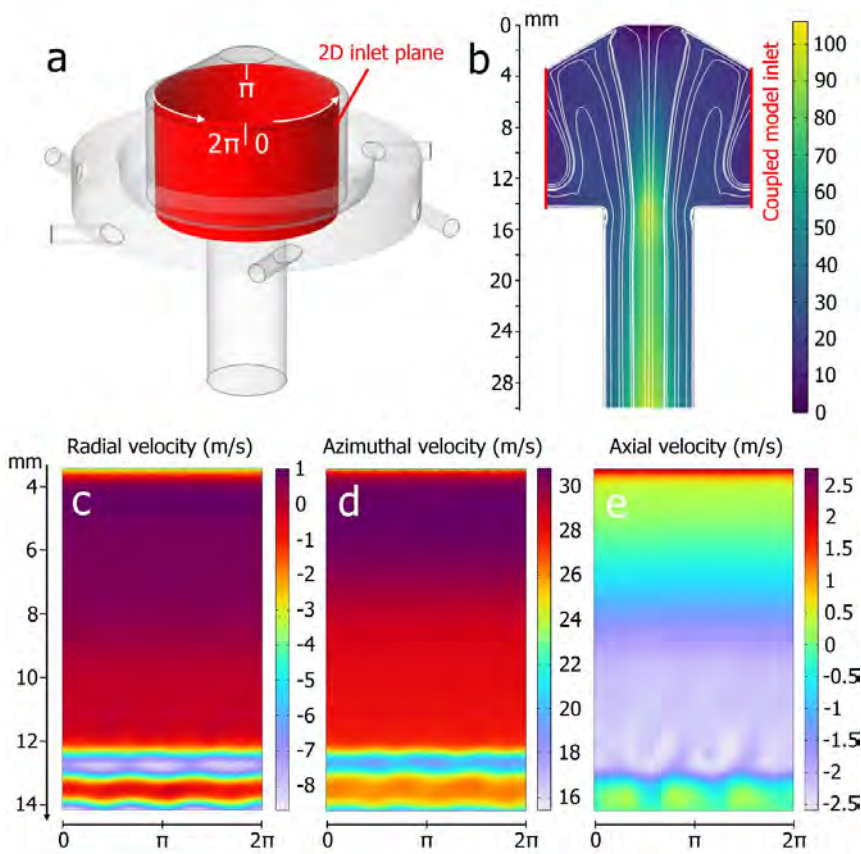


Figure 5-10 - (a) Schematic representation of the 2D inlet plane in the 3D reactor (red cylinder); 0, π , and 2π represent three values of the azimuthal angle θ . (b) Example flow profile, including streamlines for 20 SLM of a fully coupled 2D simulation; the 2D inlet line is shown in red, and corresponds to the red 2D inlet plane in panel (a). (c) Radial, (d) azimuthal, and (e) axial velocity profiles at the 2D inlet plane before averaging over θ , where 0, π , and 2π represent the positions marked in panel (a).

Figure 5-10b shows an example flow profile, including streamlines, for 20 SLM of our fully coupled 2D simulation. This result is similar to the streamlines plotted in Figure 5-9, obtained from the 3D (cold gas) flow simulation, indicating that the gas flow at the 2D model inlet can be represented by the azimuthally averaged 3D model results along the 2D inlet line.

Figure 5-10c, d, and e depict the radial, azimuthal, and axial velocity profiles at the 2D inlet plane before averaging over θ (plotted on the x-axis), respectively. While we can observe some azimuthal variation on the 2D inlet plane, originating from the separate reactor gas inlets, the variations are small; thus, azimuthal averaging for a 2D simulation is a valid approximation. The starkest differences in flow features are found in the axial velocity profile, though these absolute axial velocities are very low.

The positive radial velocities in Figure 5-10c (up to 1 m/s) can be attributed to the recirculation cell, shown in Figure 5-10b, near the 2D inlet plane. Despite the fact that converted NH_3 and hot gas would be able to leave the 2D simulation domain via the 2D inlet plane because of the outward radial flow velocity, we could define this 2D inlet plane as a boundary condition for the cold flow and 100 % NH_3 . Indeed, our fully coupled 2D simulations show negligible hot or converted NH_3 present near the 2D inlet plane or the recirculation cell near this inlet plane, justifying our approximation that decoupling the 3D flow simulations from gas heating and chemistry in the region outside the 2D model domain is valid. Note that pressure, turbulent kinetic energy, and turbulent dissipation rate are also taken as 2D model input parameters on the 2D inlet plane.

It should be noted that the turbulence parameters at the 2D inlet plane are insignificant for the 2D flow solution. Indeed, fully coupled 2D simulations with 100 times less turbulent kinetic energy than that taken from the 3D simulation at the 2D inlet plane show nearly identical flow profiles.

5.3.5 Effect of turbulence on conversion and energy cost

Figure 5-11 depicts the effect of higher or lower turbulence on the NH_3 conversion and EC as a function of SEI, for 20 SLM, by applying turbulent transport modifiers 0.2, 0.5, 1 (standard), 2, and 3.

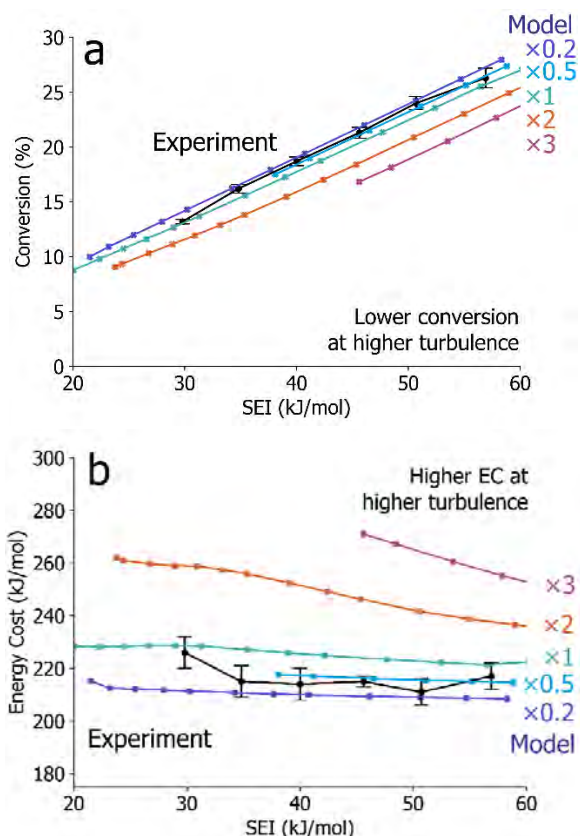


Figure 5-11 - Conversion (a) and EC (b) for 20 SLM, with turbulent transport modifiers 0.2, 0.5, 1, 2, and 3. The experimental data are plotted in black [152].

Reducing turbulence clearly increases conversion, thereby lowering EC. For instance, at an SEI of 58 kJ.mol⁻¹, the standard conversion (Figure 5-11a) is calculated as 26 %, while increasing the turbulence by a factor of 3 reduces the conversion to 23 %, and multiplying by 0.2 yields 28 % conversion. The effect on the EC (Figure 5-11b) is the opposite: at an SEI of 58 kJ.mol⁻¹, the standard EC is calculated as 221 kJ.mol⁻¹, and this value rises to 253 kJ.mol⁻¹ and drops to 208 kJ.mol⁻¹ by multiplying with a turbulent transport modifier of 3 and 0.2, respectively.

At higher turbulence, the detrimental effect on EC becomes more pronounced, and additional simulations at higher SEI (not shown) indicated that this effect remains even at higher SEI.

It should be noted that increasing the turbulence effect significantly impacts the EC, whereas increasing the flow rate does not (see Figure 5-7). This discrepancy is explained in section 5.3.7 below.

These results contrast with previous modeling work on plasma-based CO_2 conversion, which showed that enhanced diffusion (due to turbulence) improves conversion [194]. This is related to product recombination back into CO_2 when the afterglow temperature does not suddenly drop [56,158,190,203], as explained below. Also, NO_x formation from air plasmas is expected to follow the same trend [105,164]. The following sections provide insight into why higher turbulence is unfavorable for NH_3 cracking and why this differs from other gases.

5.3.6 Spatial temperature and NH_3 profiles

Figure 5-12 illustrates the spatial temperature profiles and molar fractions of NH_3 for turbulent transport modifiers $\times 3$, $\times 1$ and $\times 0.2$ at SEI of $59 \text{ kJ}\cdot\text{mol}^{-1}$. As the model is axisymmetric, the left sides of the panels represent the molar fractions, while the right sides plot the temperature profiles.

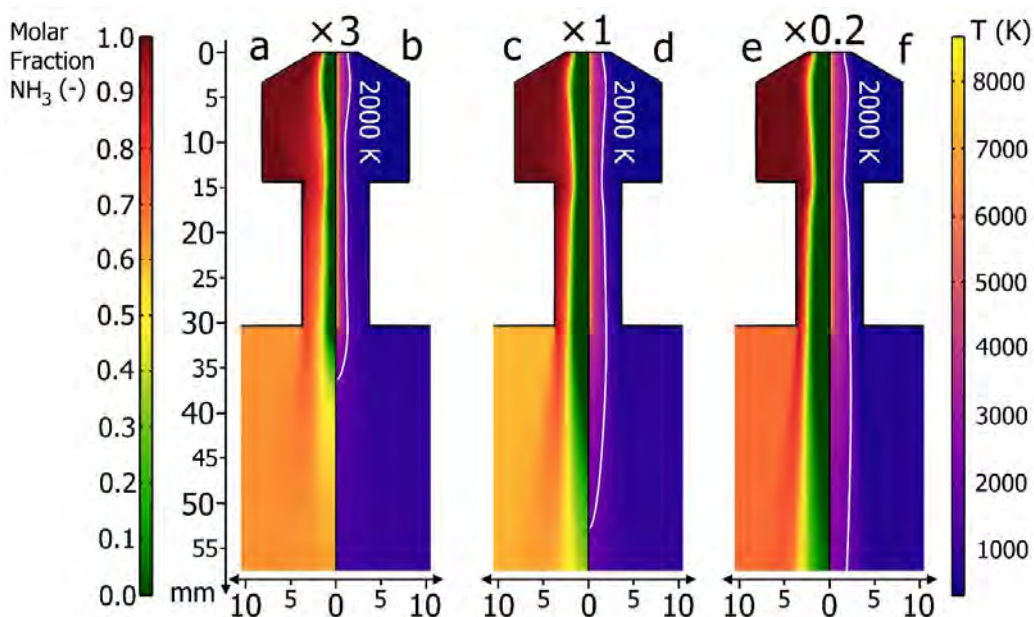


Figure 5-12 - Spatial molar fractions of NH_3 (a, c, e) and temperature profiles (b, d, f) for turbulent transport modifier $\times 3$ (a, b), $\times 1$ (c, d) and $\times 0.2$ (e, f). The 2000 K isotherm is indicated in white for each condition.

Figure 5-12b, d and f show small differences in temperature profile in the bulk plasma (i.e. 0 – 30 mm), but major differences arise in the afterglow: the hot afterglow extends further down at lower turbulence (cf. the 2000 K isotherm, which extends to 36, 52 and 72 mm for $\times 3$, $\times 1$ and $\times 0.2$, respectively). At the same time, the region of significant conversion, indicated by the lower NH₃ molar fraction, also extends much further down at lower turbulence.

Indeed, the higher temperature in the afterglow in Figure 5-12f clearly correlates with a locally lower NH₃ fraction. When comparing turbulent transport modifiers $\times 3$ and $\times 0.2$, we see that the NH₃ molar fraction at 55 mm is uniformly distributed in the former case (indicating efficient diffusional mixing after the plasma due to enhanced turbulence), whereas a distinct radial gradient remains in the latter case. Our model clearly reveals that 2000 K is sufficient to completely crack NH₃ within millisecond timescales.

It is important to note that the process of quenching in the afterglow is accelerated by turbulence. In the end, all cases reach the same mixed gas temperature at the outlet for the same SEI. This temperature is determined by the amount of cold gas present in the outer flow layer at the end of the plasma. Hypothetically, in the case that the eventual mixed temperature would be above the reactive threshold for NH₃ cracking (> 1600 K), the system would reach 100 % conversion, and turbulence would speed up the rate of conversion in the afterglow. However, this conversion would also be reached downstream (only at a bit slower rate) at low turbulence without additional energy input, so turbulence would still not be beneficial for the EC.

It should be noted here that our simulations also account for modified turbulent diffusivity for the species, as shown in equation 88. While we expected this would enhance conversion due to greater species diffusion, our model reveals that this effect is negligible under the conditions studied, compared to the effect of turbulent thermal conductivity on the temperature profile, particularly in the afterglow.

5.3.7 Changes in conversion and EC in the afterglow

To evaluate whether the elongated afterglow (in Figure 5-12f) effectively results in higher conversion, we plot in Figure 5-13 the fraction of gas above 2000 K, as well as the conversion and EC, as a function of distance from the top of the plasma reactor, following the general flow direction, at an SEI of 59 kJ.mol⁻¹, for the turbulent transport modifiers $\times 0.2$, $\times 1$ and $\times 3$. Note that the fraction of gas above 2000 K is calculated from the flow velocity as follows:

$$Fraction > 2000 K = \frac{\int_0^{R_C} 2\pi r \cdot v_z \cdot \rho dr}{\int_0^R v_z \cdot \rho \cdot 2\pi dr} \quad [94]$$

Here, R_C is the radius to the r-position where the temperature is 2000 K and R is the total radius.

In this discussion, we consider, for simplicity, that the reactor can be divided into a region with full chemical conversion (> 2000 K) and a cold region without conversion (< 2000 K), with species exchange between them determining the total conversion. It should, however, be noted that there exists a small region with a temperature ranging from 1900 K to 2100 K, where the kinetic reaction time is of the same order of magnitude as the gas residence time (~ 10 ms), and thus, the gas residence time could govern the conversion. Nevertheless, this region (1900 – 2100 K) only accounts for ~ 5 % of the overall conversion (in relative terms, i.e., ~ 1.5 % conversion in the case of 30 % overall conversion) for the different turbulent transport modifier factors or conditions investigated (i.e., 5.4 % for $\times 0.2$, 5.3 % for $\times 1$ and 5.1 % for $\times 3$). Therefore, our model reveals that changes in conversion are not due to changes in residence time but rather to changes in the length of the hot afterglow.

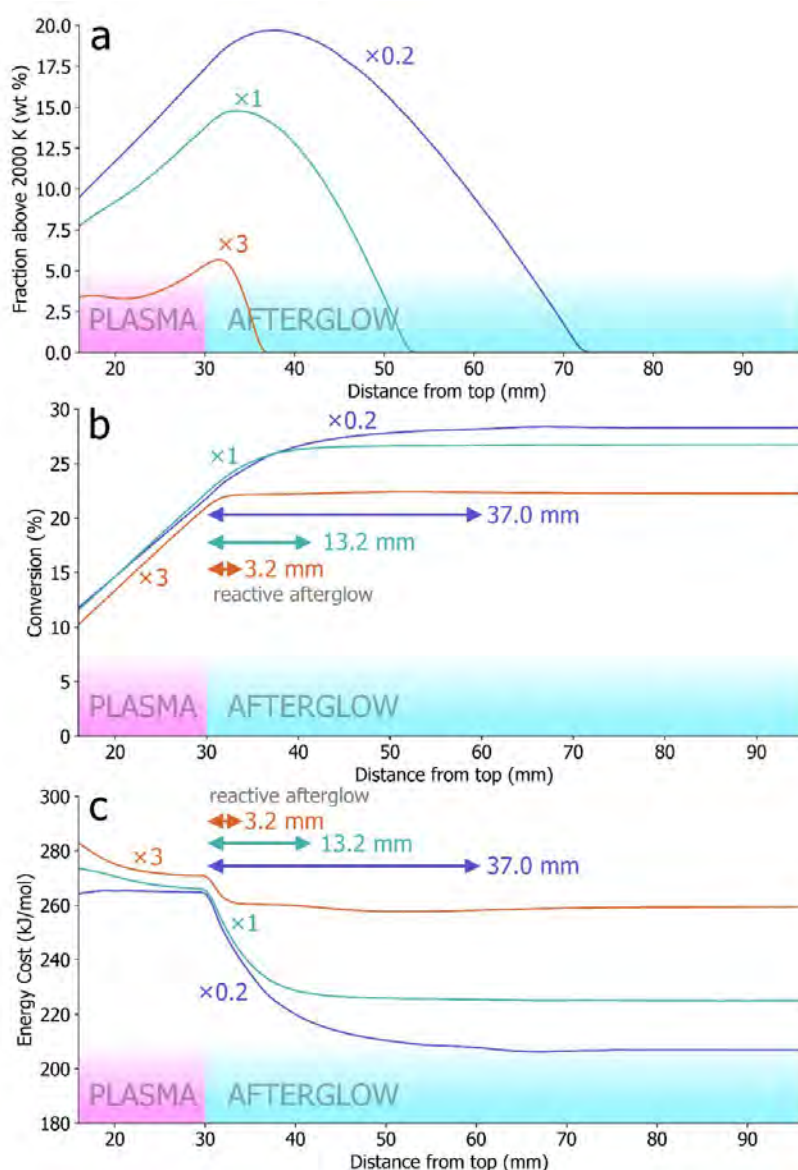


Figure 5-13 - Weight fraction of the gas above 2000 K (a), radially integrated conversion (b), and EC (c) as a function of distance from the top of the reactor, for turbulent transport modifiers $\times 0.2$, $\times 1$ and $\times 3$, at 20 SLM flow rate of NH₃ with SEI of 59 kJ.mol⁻¹. The numbers next to the arrows in (b) and (c) indicate the length of the “reactive afterglow” (where further NH₃ conversion takes place) for the three different turbulent transport modifiers.

First, in line with Figure 5-12 (higher afterglow temperature at lower turbulence), Figure 5-13a reveals that the fraction of gas above 2000 K is also clearly higher at lower

turbulence, both in the plasma and afterglow. Indeed, the fraction above 2000 K at high turbulence is very low, due to the higher thermal conductivity associated with turbulence, which leads to faster cooling and thus a lower gas fraction above 2000 K.

Second, as illustrated in Figure 5-13b, the turbulent transport modifier does not seem to affect the NH_3 conversion in the plasma, despite the smaller fraction of gas above 2000 K at high turbulence. Indeed, inside the plasma reactor, higher turbulence is actually beneficial because it promotes more mixing of the gas species, i.e., diffusion of unreacted NH_3 into the hot (above 2000 K) plasma zone, as well as diffusion of H atoms out of this zone towards the cooler surroundings, where it reacts with unconverted NH_3 , as shown in section 5.3.3. This improved mixing leads to higher overall conversion. This effect compensates for the smaller weight fraction of gas above 2000 K, and therefore, the conversion with turbulent transport modifiers $\times 3$, $\times 1$ and $\times 0.2$ matches at the end of the plasma in Figure 5-13b. Importantly, our model reveals that the conversion attributed to H atom diffusion from the plasma center towards cold NH_3 is significant but not the major contributor compared to NH_3 diffusion into the hot plasma zone.

In contrast to the conversion inside the plasma, the afterglow shows a lower turbulent transport modifier, further increasing the conversion. This “free conversion” (i.e., without extra plasma power) in the hot afterglow (above 2000 K) is due to cracking of NH_3 , which did not pass through the hot plasma core. Hence, a longer hot afterglow, as shown in Figure 5-12f, leads to more “free conversion”. The length of this “reactive afterglow” is indicated in Figure 5-13b and is inversely related to the strength of turbulence.

The effect is even more pronounced for the EC (Figure 5-13c): while the EC at the end of the plasma is more or less independent of the turbulent transport modifier, the additional conversion without extra plasma power in the afterglow at limited turbulence ($\times 0.2$) results in a significant drop in EC. If turbulent species diffusivity were important under the conditions studied, it would show a clear drop in EC for higher turbulent transport modifiers; however, we do not observe this effect because the effect of turbulent thermal conductivity on the temperature profile is more dominant.

This is important in order to understand the different behavior between Figure 5-13 and Figure 5-7. The classical formulation of the Reynolds number would suggest that increasing the flow rate will increase turbulence; however, the EC at 10 SLM and 20 SLM is the same (see Figure 5-7). Our model clarifies this by finding increased turbulence at the inlet, but equal turbulence in the afterglow. Figure 5-13 shows that the effect of

turbulence on conversion and EC is only important in the afterglow, so any change in turbulence at the inlet does not affect conversion and EC.

In essence, our turbulence model confirms our pin-to-pin arc plasma modeling insights that increased H atom diffusion improves the NH₃ conversion inside the plasma, but the overall effect of enhanced turbulence is actually detrimental for the conversion performance, due to excessive cooling in the afterglow. Indeed, the highest overall conversion is achieved at the lowest turbulence level.

Furthermore, the conclusions obtained from Figure 5-13 can also be observed in the integrated energy balance. Figure 5-14 illustrates this energy balance for the conditions of Figure 5-13, integrated over distance from the top of the reactor.

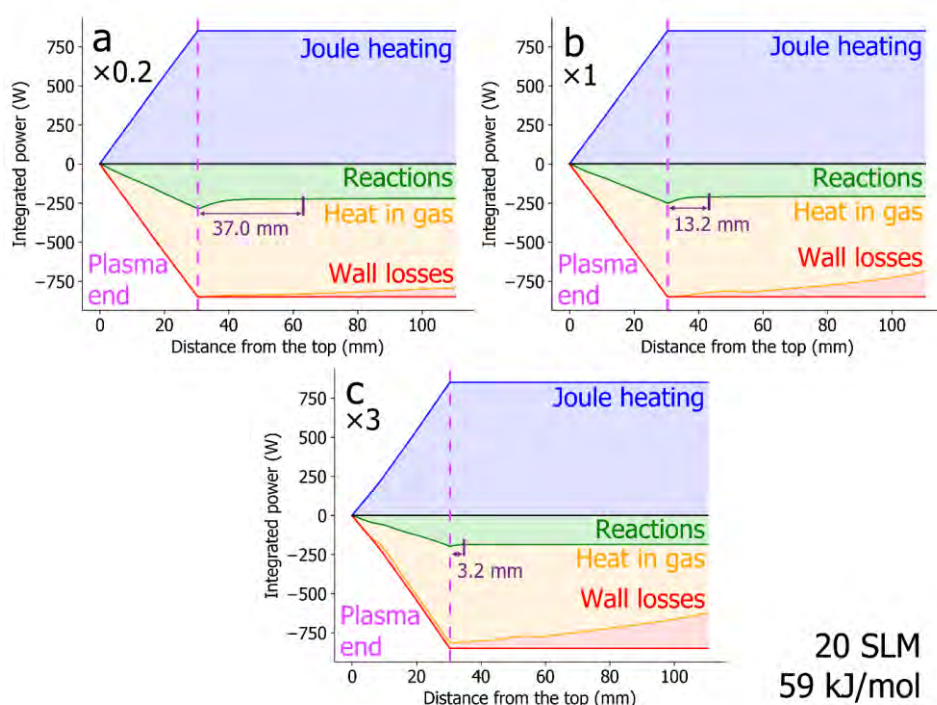


Figure 5-14 - Integrated power over distance from the top of the reactor, with one source term (Joule heating, in blue), and various sink terms, namely chemical reactions (green), heat stored in the gas (orange), and heat losses at the walls (red), for turbulent transport modifiers $\times 0.2$ (a), $\times 1$ (b) and $\times 3$ (c), at 20 SLM flow rate of NH₃ with SEI of 59 kJ.mol⁻¹. The end of the plasma (at 30 mm) is indicated with a pink dashed line. The small vertical purple line indicates where chemical reactions have stopped.

Indeed, Figure 5-14 demonstrates a similar effect of the reactive afterglow. First of all, the decomposition of NH₃ becomes exothermic above 1230 K. Hence, the net NH₃

cracking means that in the energy balance, the energy from chemical reactions is transferred to gas heating. Indeed, the chemical reactions release heat to the gas in the afterglow (the green area slightly drops and the orange area slightly rises in Figure 5-14, in the region where chemical reactions still occur in the afterglow, indicated by the horizontal purple arrow). This is somewhat more pronounced for a lower turbulent transport modifier ($\times 0.2$) and somewhat less pronounced for a higher one ($\times 3$). This small difference in Figure 5-14 has the same effect as the difference in conversion (and corresponding EC) shown in Figure 5-13 for the different turbulent transport modifiers. While the effect might seem more pronounced in Figure 5-13c, this is only due to the y-axis (ranging from 180 (instead of 0) to 300 kJ.mol⁻¹ in Figure 5-13c).

Overall, the energy balance indicates that the energy input (from Joule heating) primarily goes into gas heating and chemical reactions (which further heat the gas in the afterglow, as NH₃ cracking is exothermic), while wall heat losses are minimal. Although there is greater heat loss to the walls with increased turbulent transport due to additional heat transfer (cf. Figure 5-14c vs. Figure 5-14a), our simulations indicate that these losses have a negligible effect on conversion (and EC). Indeed, wall heat losses only become significant after chemical reactions have stopped, as indicated by the small purple vertical line, because the temperature is below the threshold for chemical reactions (~ 2000 K) within the typical gas residence time in the reactor (~ 10 ms). Therefore, even if energy losses to the walls become important later in the afterglow (for a higher turbulent transport modifier factor), this will not affect conversion, as no gas is above 2000 K anyway (see Figure 5-12).

5.3.8 Future reactor design from modeling insights

Combining Figure 5-12, Figure 5-13, and Figure 5-14, we can conclude that while H atom diffusion helps to improve the NH₃ cracking performance inside the plasma, trying to exploit this mechanism by enhanced turbulence is actually counterproductive. Indeed, the additional cooling in the afterglow due to higher turbulence is detrimental to the overall NH₃ conversion.

Thus, while afterglow cooling is beneficial for CO₂ conversion or NO_x production from air plasmas, the mechanism is completely different for NH₃ cracking. For CO₂ conversion and NO_x production, slow cooling in the afterglow leads to recombination of the products (CO + O/O₂ or NO + O/N) back into the feed gas (CO₂ or N₂/O₂), thereby limiting overall conversion. Therefore, fast quenching of the products to lower temperatures is needed to retain the conversion [105,194–197,204]. The situation is completely

opposite for NH₃ cracking. Indeed, the NH₃ kinetics do not need to be quenched to retain the products, and in contrast, a higher afterglow temperature is beneficial for additional “zero cost” conversion.

Finally, our calculations reveal that still higher temperatures in the afterglow (above 2000 K) do not yield further improvement in conversion and EC. Indeed, 2000 K is sufficient to completely crack NH₃ within timescales of milliseconds. The key is thus to keep a temperature around 2000 K for as long as possible in the afterglow, but higher temperatures do not lead to additional gains.

Overall, our modeling insights reveal that a small forward vortex flow is required to stabilize the plasma, but a strong (reverse) vortex should be avoided to minimize turbulence (when the circumferential flow speed becomes comparable to the axial flow speed). The key is to extend the hot afterglow as much as possible by employing a long afterglow gas chamber. The afterglow chamber should not be wider than the plasma chamber, to avoid forced mixing and thus quenching. Therefore, we expect that warm plasmas with only a forward vortex, such as microwave plasmas (which operate without electrodes and can accommodate an extended hot afterglow) or DC arc plasma torches with a long afterglow chamber, should lead to further improvement. This should be investigated in future work.

5.4 Conclusion

We developed a CFD model that integrates gas-flow dynamics (turbulent flow), heating, current conservation, species transport, and chemistry for NH₃ cracking in a warm plasma reactor, demonstrating good agreement with experimental data.

Specifically, we found that turbulence reduces NH₃ conversion and increases EC. This effect is striking because it contrasts with observations for CO₂ splitting and NO_x formation by warm plasmas [105,194–197,204]. Analysis of our model results indicates that turbulence suppresses a hot afterglow. While fast afterglow quenching is beneficial for plasma-based CO₂ splitting and NO_x production from air plasmas to avoid recombination of the products, the NH₃ kinetics do not suffer from recombination reactions at typical plasma afterglow conditions, and in contrast, they benefit from “free” NH₃ conversion (without extra plasma power) in an extended hot afterglow. Based on our modeling insights, we propose using plasma reactors with a long afterglow chamber of the same width as the plasma chamber to further improve the performance of warm plasma-based NH₃ cracking.

Chapter 6

Two-zone global model of a CH₄ nanosecond pulsed plasma

The content of this chapter is in part based on:

Tuning product selectivity in CH₄ nanosecond pulsed plasma: Insights in the reaction pathways by a two-zone global plasma model.

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and

Time-dependent optical measurements and modelling of CH₄ nanosecond pulsed plasma

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Submitted to Plasma Sources Science and Technology.

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We developed a two-zone global plasma model to investigate the formation pathways of C₂ hydrocarbons and H₂ in a CH₄ nanosecond pulsed plasma. The model not only solves the classical species mass balance equations but also the energy balance equations for heavy species, and accounts for mass and energy exchange, including gas heating and pressure rise during the plasma pulse. Our results reveal that the interplay between gas temperature and electron-impact dissociation critically influences product selectivity. Longer pulse durations favor the formation of unsaturated hydrocarbons, whereas shorter pulse durations promote more saturated products. Excessively long pulses, however, lead to significant electron-impact dissociation of C₂H₂, which may contribute to soot formation. Preheating the gas mixture for short (< 30 ns) pulse durations shifts selectivity toward C₂H₄ and C₂H₂. These insights highlight the importance of pulse parameters and preheating strategies for controlling product selectivity in nanosecond-pulsed plasmas.

6.1 Introduction

As stated in Chapter 1, H₂ production research focuses on CH₄ pyrolysis, which produces carbon black (or other carbon-based materials) as a byproduct rather than CO₂. Industrial steam reforming of methane (SMR) exhibits a low production cost, namely \$ 2.08 per kg H₂, and an operating EC of 141 MJ.kg⁻¹(H₂) or 284 kJ.mol⁻¹(H₂), including heating, cooling, and heat exchange costs [8,205]. Patlolla et al. stated that current CH₄ pyrolysis technologies can produce H₂ at an EC similar to SMR while cutting CO₂ emissions by 75 % [206]. However, further improvements should be made in the longevity of pyrolysis reactors to ensure high H₂ yield while maintaining high-quality carbon products [206,207]. Furthermore, the upcycling of solid carbon is an issue, as demand for H₂ far exceeds that for solid carbon products [208]. This issue cannot be solved via classical high-temperature pyrolysis. It is known that solid carbon products are thermodynamically more stable than smaller hydrocarbons, even up to 3000 K [209]. Hence, prolonged high-temperature treatment of CH₄ shifts the reaction pathway from the formation of C₂ hydrocarbons (C₂H₂, C₂H₄, C₂H₆), which act as intermediates, toward their further conversion into solid carbon and H₂ [210].

This limitation is the main motivator for CH₄ splitting via non-thermal plasmas. Various plasma setups have already been explored for CH₄ splitting, aiming to optimize product yields. H₂ production from CH₄ typically proceeds in thermal plasmas. For instance, Fulcheri et al. [31] achieved >99 % CH₄ conversion and >95 % H₂ selectivity using a thermal plasma pyrolysis setup. Furthermore, Kim et al. [33] developed a DC-RF thermal plasma setup for pyrolysis to crystalline carbon and H₂, while Mašláni et al. [32] reported high selectivity towards H₂ and carbon black using a thermal steam plasma.

Next to H₂, C₂ hydrocarbons (C₂H₂, C₂H₄, C₂H₆) can also be targeted in CH₄ plasmas, where C₂H₂, C₂H₄, and C₂H₆ are typically promoted in different plasma types. For instance, Kado et al. [211] used a periodic pulsed spark discharge to optimize C₂H₂ production, reaching 95 % selectivity and 52 % CH₄ conversion. Bilera et al. [212] published a review paper reporting an optimal CH₄ conversion of 90 % with 80 % selectivity towards C₂H₂. Optimization of C₂H₆ production was achieved by De Felice et al. [213] using a dielectric barrier discharge (DBD), reaching 59 % selectivity. Indeed, C₂H₆ is the major product in DBD plasma reactors for CH₄ conversion [17,214,215]. Finally, some papers also reported optimization towards C₂H₄, which is the hydrocarbon product with the highest commercial value [216–218]. For instance, Liu et al. [216] reached 68 % selectivity of C₂H₄ at 32 % CH₄ conversion in a hybrid plasma-thermal reactor. Their two-stage reactor

was optimized for C₂H₄ by placing a thermal cracking reactor at 880 °C after a cylindrical DBD reactor producing mainly C₂H₆ and C₃H₈.

Delikonstantis et al. [217] reported optimization of C₂H₄ production in another two-stage reactor, with the first stage being a nanosecond (ns) pulsed plasma, creating mainly C₂H₂. Afterward, a Pd-based catalyst converts C₂H₂ into C₂H₄ in the post-plasma zone. The authors reported a C₂H₄ yield of 23.5 % per pass, based on 80 % selectivity and a CH₄ conversion of 29.4 %. While conceptually very interesting, the EC was 1.64 MJ.mol⁻¹ C₂H₄, which is too high to be industrially relevant, as the EC should be close to or below 1 MJ.mol⁻¹ C₂H₄, because steam cracking of C₂H₆ operates at 560 – 840 kJ.mol⁻¹ C₂H₄ [219]. However, a real comparison of both processes should also take into account the absence of CO₂ emissions in plasma reforming and the different feedstocks, but this is beyond the scope of this chapter.

Fortunately, CH₄ conversion also produces two H₂ molecules per C₂H₄ formed out of two CH₄ molecules. As mentioned above, industrially, H₂ is nowadays still mainly produced by SMR, at an EC of 284 kJ.mol⁻¹(H₂), including heating, cooling, and heat exchange costs [205]. This translates to an EC of 568 kJ.mol⁻¹ CH₄ converted. Thus, if we can optimize the product composition to be shifted from solid carbon to higher-value C₂ hydrocarbons (preferably C₂H₄) combined with H₂, plasma-based CH₄ conversion could be an industrially interesting approach to both H₂ and C₂H₄ production. Combining the EC for H₂ and C₂H₄ production and considering that separation costs are a major part of the overall process EC [72,220], we believe that an EC of 1.56 MJ.mol⁻¹ C₂H₄ or 780 kJ.mol⁻¹ CH₄ converted with 100 % C₂H₄ selectivity should be the upper limit for plasma-based CH₄ conversion into both H₂ and C₂H₄, to be industrially relevant. Note that this indeed requires 100 % selectivity towards C₂H₄, as separation costs, not only from C₂H₆ but also leftover CH₄, are not considered in this value. Especially, C₂H₆ separation is the dominant cost, since it is performed cryogenically, and thus, the major goal should be to almost completely avoid C₂H₆ production [72,157,220,221].

Following the above literature overview, the most promising approach for plasma-based non-thermal CH₄ cracking towards C₂ hydrocarbons (especially C₂H₄) and H₂ is given by ns-pulsed plasmas, as they exhibit a lower experimental EC, in the range of 400 kJ.mol⁻¹ CH₄ converted [71,217,222,223]. Note, however, that these EC values obtained were for a product mix of mainly C₂H₂, followed by C₂H₄ and a smaller amount of C₂H₆, and thus, the overall EC towards pure C₂H₄ and H₂ production, including product separation costs, would be much higher.

Quite a few researchers have already studied ns-pulsed CH_4 plasma, including the effects of pulse length, frequency, and pressure on the relative importance of thermal vs. electron-impact CH_4 dissociation and C_2 product selectivities. Some noteworthy observations include the following. Gao et al. [224] demonstrated that the effect of thermal conversion, in contrast to electron-impact dissociation, increases with pulse length when comparing ns- and μs -pulsed discharges. Furthermore, Delikonstantis et al. [218] reported an optimized pulse frequency for unsaturated hydrocarbons, as gas heating from the pulses shifts the selectivity of the C_2 hydrocarbons towards C_2H_2 . Van Rompaey et al. [70,71] studied the effect of pressure on the CH_4 conversion and resulting C_2 selectivities, but did not observe a significant shift in selectivity when scanning from 0.5 to 2 atm, while their energy efficiency tripled over the same pressure increase. Finally, Van Rompaey et al. [71] also modeled the relative importance of thermal and electron-impact CH_4 dissociation. By applying a set temperature profile (not self-consistently calculated, but obtained from their experiments), they found that electron-impact collisions dissociate less than 50 % of the CH_4 at the start of the pulse, while thermal reactions dissociate the majority of CH_4 at later times during (and after) the pulses. Altogether, these studies reveal that the interplay between gas temperature and electron-impact kinetics in ns-pulsed plasmas is crucial for optimizing CH_4 conversion into various C_2 hydrocarbons and H_2 , and that a better understanding of this chemical interplay is needed for further optimization.

This chapter aims to improve our understanding of this interplay by developing a model for ns-pulsed plasmas that not only describes the plasma chemistry but also solves the heavy species energy balance. Thus, it avoids the need for a user-defined temperature profile, as in previous work [71], but allows for self-consistent calculation, which should give more accurate insights. Ideally, this should be investigated using a multidimensional model of the CH_4 ns-pulses, including the coupled solution of the streamer dynamics via the Poisson equation and the species continuity equations, as e.g., presented for air plasma with a much smaller chemistry set, consisting of ca. 100 reactions [129–132,225,226]. Unfortunately, the CH_4 plasma chemistry is too complex for this to be computationally feasible. Instead, we developed a two-zone global plasma model, in which a central plasma zone solves the plasma kinetics, including the electron energy balance, and a cold surrounding zone serves as a reservoir for cold plasma species. Both zones are described by global models that feature continuous, system-dependent species and energy exchange rates. Furthermore, we validate this model by comparing the calculated C_2 hydrocarbon selectivities with experimental data. With this model, we

aim to expand the global modeling approach currently used in the literature [48,68,71,95,125,227,228], which typically relies on user-defined temperature profiles as input, toward a more self-consistent method. In addition, we use this model to better understand the thermal effects of ns-pulsed plasmas on product selectivities and the underlying chemistry by scanning over various pulse energies and, for fixed pulse energies, various initial gas temperatures.

6.2 Computational details

Our two-zone model consists of a global plasma model and a global thermal kinetics model. The global plasma model is built within the COMSOL plasma module [123], while the global thermal kinetics model is built within the COMSOL chemical reaction engineering module. All equations were presented in Chapter 2. The experiments used for model validation can be found in [124].

6.2.1 Inferred spatial dimensions

The 0D model is applied to two connected global reservoirs, as shown in Figure 6-1. The plasma domain solves species densities, gas temperature, and electron temperatures. The cold domain solves the species densities and gas temperature. All equations describing these can be found in Chapter 2. As stated there, the plasma radius is set to 0.25 mm.

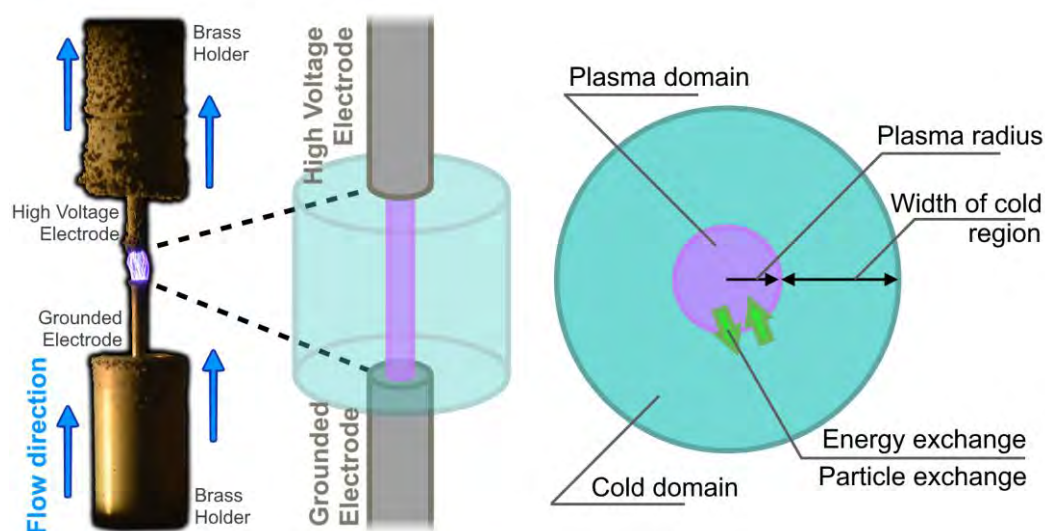


Figure 6-1 - Picture of the discharge and electrodes (left), and schematic representation of the 0D modelled domains (center and right).

As can be seen from Figure 6-1, this system suffers from soot formation. Soot attaches at the top electrode mostly due to the flow as the wide spacing in between the very short pulses does not allow for electromagnetic effects to come into play.

6.2.2 Calculations of product selectivities

To validate our model, we compare our calculated (carbon-based) product selectivities with our experimental data at the same conditions:

$$S_{C_2H_x} = \frac{2n_{C_2H_x_{end}}}{n_{CH_4_{start}} - n_{CH_4_{end}}} \quad [95]$$

Here, $n_{C_2H_x_{end}}$ is the final molar amount of a species C_2H_x in the total system, including both cold and plasma zone (mol), and $n_{CH_4_{start}}$ and $n_{CH_4_{end}}$ are the total amount of CH_4 in the system (mol), at the start and end of the simulation.

6.2.3 Chemistry set

Table 6-1 lists the species included in the model, in addition to electrons. The plasma zone considers all species, while the cold zone does not consider the ions, electrons, and the vibrationally excited species, as they are negligible here [48,71].

Table 6-1 - Neutral species, ions, electronically and vibrationally excited species included in the model, besides the electrons. More information about the notation of electronically and vibrationally excited states can be found in spectroscopy literature [229–231]. The plasma domain includes all neutrals, ions, electrons, electronically and vibrationally excited states, while the cold domain only includes neutrals and electronically excited states.

<i>Species</i>	H_x	CH_x	C_2H_x
<i>Neutrals</i>	H, H ₂	C, CH, CH ₂ , CH ₃ , CH ₄	C ₂ , C ₂ H, C ₂ H ₂ , C ₂ H ₃ , C ₂ H ₄ , C ₂ H ₅ , C ₂ H ₆
<i>Ions</i>	H ⁺ , H ₂ ⁺ , H ₃ ⁺ , H ⁻	C ⁺ , CH ⁺ , CH ₂ ⁺ , CH ₃ ⁺ , CH ₄ ⁺ , CH ₅ ⁺	C ₂ ⁺ , C ₂ H ₂ ⁺ , C ₂ H ₃ ⁺ , C ₂ H ₄ ⁺ , C ₂ H ₅ ⁺ , C ₂ H ₆ ⁺
<i>Electronically excited states</i>	H(2s), H(2p), H(n=3)	C(¹ D), C(¹ S), CH(⁴ a), CH(² A), CH(² B), CH ₂ (¹ A), CH ₂ (¹ B)	
<i>Vibrationally excited states</i>	H ₂ (v1 – v14)	CH ₄ (v2,v4), CH ₄ (v1,v3)	C ₂ H ₂ (v5), C ₂ H ₂ (v2), C ₂ H ₂ (v3,v1), C ₂ H ₄ (v1), C ₂ H ₄ (v2), C ₂ H ₆ (v2,v4), C ₂ H ₆ (v1,v3)

The full set of chemical reactions can be found in the Supporting Information of our paper [232].

6.3 Results and discussion

First, we will present key variables calculated by our model that affect the chemical kinetics discussed later. Then we will compare our calculated product selectivities with experimental data for model validation. Subsequently, we will analyze the reaction pathways for different pulse energies (or durations) to explain the difference in product selectivities. Finally, based on our modeling insights into the delicate interplay between thermal and electron-impact reactions and how this is influenced by pulse duration, we will explore how to tune product selectivities and reduce EC through gas preheating under different pulse conditions.

Based on our experiments, we selected five conditions with distinct pulse energies, as listed in Table 6-2. A Gaussian is fitted to the experimental data, keeping the energy per pulse constant.

Table 6-2 - Pulse energies, FWHM, and amplitude of the pulses, for five different conditions.

<i>Condition</i>	<i>Pulse Energy (mJ)</i>	<i>FWHM of the pulse (ns)</i>	<i>Amplitude (kW)</i>
<i>A</i>	1.37	22	56
<i>B</i>	2.24	21	100
<i>C</i>	4.80	32	141
<i>D</i>	5.74	38	137
<i>E</i>	6.27	39	152

6.3.1 Key variables as a function of time

Figure 6-2 depicts the power density profile as a function of time, used as input in the model, for the five different pulse conditions, obtained from our experiments [124], as well as the calculated pressure, gas temperature, and CH₄ conversion, as a function of time during and after one pulse. The pulses start at 100 ns to ensure the system starts from a fully relaxed state.

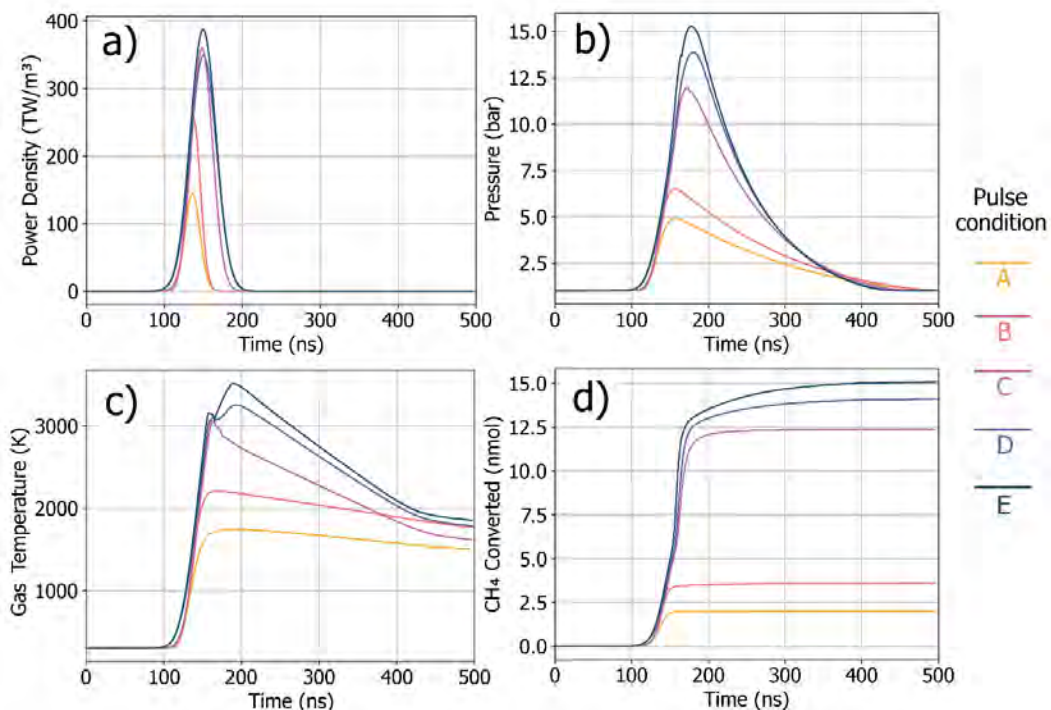


Figure 6-2 - Input power density (a), and calculated pressure (b), gas temperature (c) and CH₄ conversion (d), as a function of time, during and after one pulse, for five different pulse conditions (A, B, C, D and E; see Table 6-2).

The shape of the power density pulse (Figure 6-2(a)) is a Gaussian fitted to the measured power deposition, then divided by the plasma volume. The original measured power profiles are presented by Fontaine et al. [124]. We can distinguish two groups: condition A and B (with lower FWHM) on the one hand, and conditions C, D, and E (with similar peak powers and FWHM) on the other hand. For simplicity, we will refer to them as the short-pulse group (conditions A and B) and the long-pulse group (conditions C, D, and E).

Figure 6-2(b) indicates the significant pressure increase in the plasma volume, to 4.9 bar for condition A, and up to 15.3 bar for condition E. This can be explained by a combination of three effects. The first effect is the dramatic rise in gas temperature (Figure 6-2(c)), which reaches 1700 K and 3400 K, for pulse conditions A and E, respectively. As the plasma volume is considered to be constant here [129,130], in a theoretically closed system, a rise in temperature from 300 K to 1700 K would give rise to a factor 5.7 increase in pressure, based on the ideal gas law. The second effect is due to chemical reactions, where either electron-impact or thermal dissociation of CH₄ yields

two particles (CH₃ and H) from CH₄, hence doubling the number of particles in the case of complete dissociation. In reality, there is no complete dissociation, but the increase in the number of particles also explains the rise in pressure. The last effect reduces the impact of the previous two effects, as gas species can leave the plasma zone, following the pressure-driven mass-exchange equations, until equilibration with the cold zone is reached. The combination of these three effects leads to the rise in pressure observed in Figure 6-2(b), which indicates that the first two effects dominate at the pulse start, resulting in the observed very high pressure peak, after which the pressure-enforced exchange with the surrounding colder zone equilibrates the system within the time scale of a few 100 ns.

Figure 6-2(c) illustrates the calculated temperature profiles for all pulse conditions. We can observe a clear distinction between the short pulse group, on one hand, yielding a peak temperature of 1700 K and 2200 K for conditions A and B, respectively, and the long pulse group, on the other hand, which exhibits an initial peak of 3000 K, followed by a temperature drop for condition C, while the temperature increases further for conditions D and E.

This initial peak of 3000 K in the case of the longer pulse group is attributed to complete dissociation via either electron-impact or thermal reactions with CH₄. Subsequently, energy from electron-impact collisions is stored in excited states (of CH₂ and CH; see Table 6-1), which is released after a few ns via heavy species collisions, explaining the further temperature rise. However, as is clear from Figure 6-2(c) for conditions D and E, this is only a very small amount of energy.

This effect of CH₄ dissociation on the temperature profiles can also be observed from the changing slopes in Figure 6-2(d). The initial slope at 120 ns is due to electron-impact dissociation of CH₄. All pulse conditions initially exhibit the exact same slope in CH₄ dissociation. However, the short pulse group yields incomplete conversion in the plasma zone. Indeed, the lowest molar fraction of CH₄ in the plasma zone is 85 % and 68 % for conditions A and B, respectively, while it is less than 3 % for the other pulse conditions with higher energy and longer pulse duration. This explains why the short-pulse group reaches saturation early, while the other pulse conditions continue converting CH₄ at the same rate. The latter leads to additional gas heating, as observed in Figure 6-2(c), and this high gas temperature allows for optimal use of any remaining radicals after the pulse, which will convert more CH₄ during the afterglow, both in the plasma zone and in the colder surrounding zone, as we will discuss in section 6.3.3.

6.3.2 Product selectivities for model validation

Figure 6-3 illustrates the calculated and experimental C_2H_x selectivities for the five different pulse conditions.

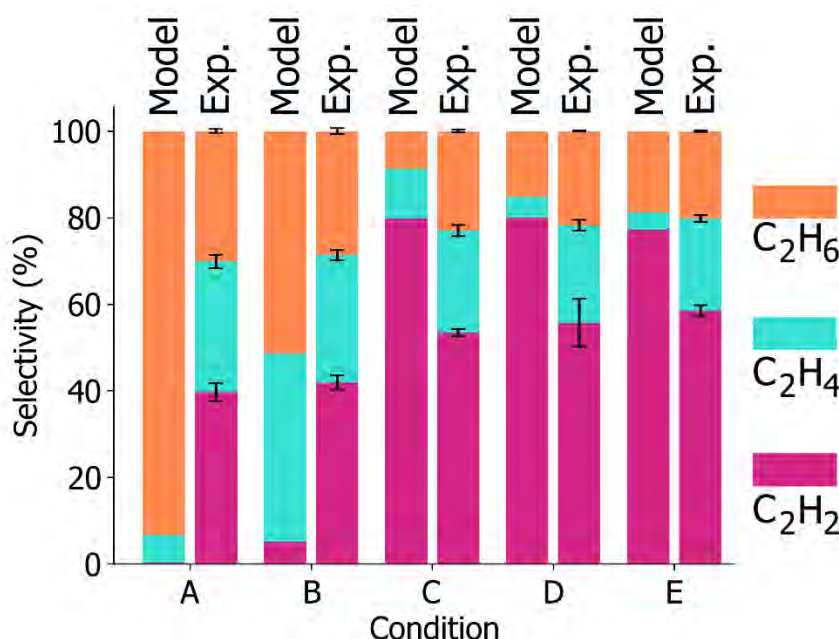


Figure 6-3 - Calculated and experimental C_2H_x selectivities for the five different pulse conditions.

The calculated trend shown in Figure 6-3 is very pronounced, with the short and long pulse groups leading to more C_2H_6 and C_2H_2 , respectively. Indeed, while condition A predominantly yields C_2H_6 and no C_2H_2 at all, the C_2H_2 selectivity rises to 75 - 80 % for the longer pulse group. On the other hand, the largest selectivity for C_2H_4 (43 %) is predicted at condition B.

The experimental results show the same trend, although much less pronounced. The C_2H_2 selectivity at condition A is 40 %, and it increases to 55 - 60% for the long pulse group, while the C_2H_6 selectivity decreases from 30 % to 20 %, comparing condition A and E.

It is known that higher gas temperatures favor unsaturated hydrocarbon formation over saturated hydrocarbons [71,209]. The discrepancy between model and experiment can therefore be attributed to a mismatch in the calculated plasma temperature. The latter can be due to either changes in plasma radius for different pulse conditions, while it is

fixed at 0.25 mm in our model, or due to changes in the plasma behavior. Indeed, the imaging in our experiments shows a more glow-like plasma for condition A and a more filamentary plasma for the other pulse conditions (see images in Figure 6-4) [124]. These effects cannot be captured with our global model and require a multidimensional model, which is beyond the scope of this chapter.

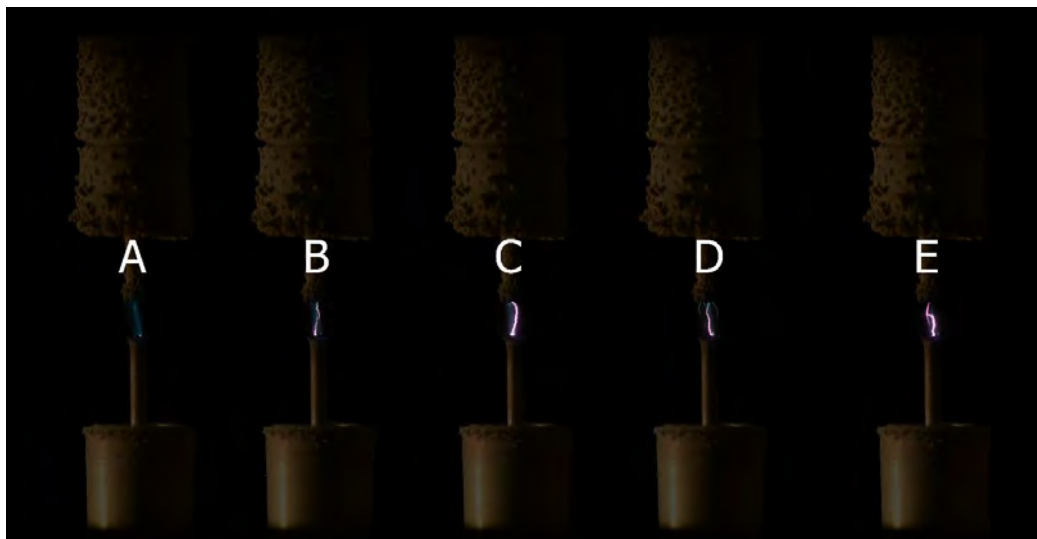


Figure 6-4 - Imaging of single experimental pulses for all pulse conditions (A, B, C, D, and E). The pins shown in the images have been added in post-processing for clarity.

The glow-like plasma can be clearly observed in Figure 6-4 for condition A, meaning that the large discrepancy in the calculated product selectivities is likely due to the very diffuse plasma behavior, which is not well captured by our two-zone model. In contrast, the other pulse conditions yield a more filamentary plasma, which is better described by our model. Indeed, the agreement with experiments is reasonable for the longer pulse durations, obviously keeping in mind the limitations of a global model. Overall, our global model provides a clear improvement indeed compared to standard global models, as it accounts for mass and energy exchange between the plasma and colder surrounding zone, and it uses only one input parameter (plasma radius), while all other plasma characteristics are calculated self-consistently; the latter is typically not the case for global models [48,71,125,228,233,234].

Following this reasoning, we will analyze the chemical pathways in section 6.3.3 for conditions B and E, which are representative of the short and long pulse groups, respectively. The long pulse group yields the best agreement with the experimental

selectivities, and while for condition A the discrepancy is quite large, condition B yields somewhat better agreement, also because the calculated gas temperature agrees quite well with earlier measurements for ns-pulsed plasmas at similar conditions, where values of ~2000 K were reported [71].

6.3.3 Chemical pathway analysis

We can explain the differences in selectivity results presented in the previous section using the reaction pathways. Figure 6-5 depicts the reaction pathway analysis for condition B, showing the evolution of species in both the plasma and cold zone. For each reaction, the co-reactant and co-product are indicated on the reaction arrow (with + and -, respectively), together with the relative contribution of that reaction in the total destruction of the considered species. If no percentage is given (a single arrow), this reaction is the only species destruction pathway. Reactions with relative contributions below 1 % are omitted, except for the initial ionization reactions, to show the dominant ions. Reactions where no co-reactant or co-product is indicated proceed with any neutral reacting species. The only final products indicated are C_2H_2 , C_2H_4 , and C_2H_6 , while H_2 is only shown as a co-product to avoid making the figure too complex. However, to clearly visualize H_2 production, we write this species in bold red each time. The major pathway is indicated, with the relative contribution (%) shown in bold, leading to the major products shown in bold red.

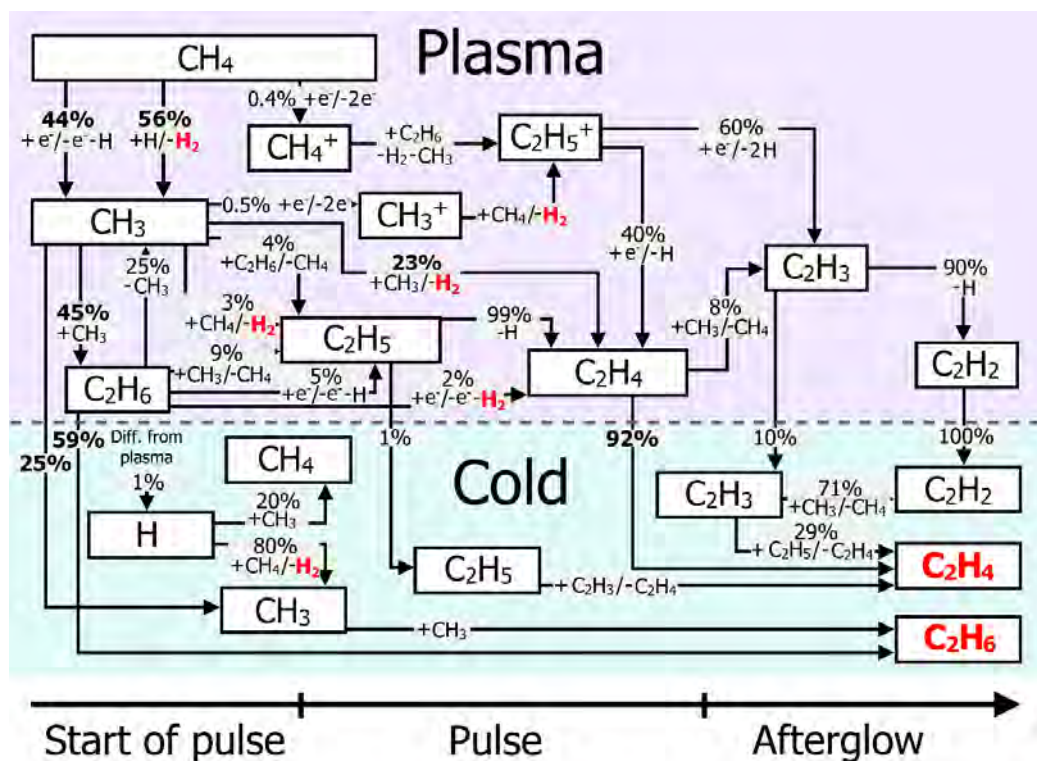


Figure 6-5 - Chemical reaction pathway analysis for condition B, showing the conversion of one species to another in both the plasma and cold zone. For each reaction, the co-reactant and co-product are indicated on the reaction arrow (with + and -, respectively), together with the relative contribution of that reaction to the overall destruction of the considered species. If no percentage is present (a single arrow), this reaction is the only species destruction path. Reactions with relative contributions below 1 % are omitted, except for the initial ionization reactions to show the dominant ions. The major pathway is indicated with the relative contribution (%) shown in bold, leading to the major products shown in bold and red. H₂ as a co-product is indicated in bold, red font each time.

Figure 6-5 also provides time information, going from left to right. Starting at the top left corner, CH₄ is present in the plasma at the start of the pulse. The first reactions occurring are ionization of CH₄ (0.4 %), creating more electrons as well as CH₄⁺ ions, and electron-impact dissociation of CH₄ (44 %), creating CH₃ and H. A small fraction (0.5 %) of the formed CH₃ radicals is also ionized to CH₃⁺. These are the two dominant ions in the early stages of the pulse. The H atoms produced by electron-impact dissociation of CH₄ will further dissociate some CH₄ (56 %), forming additional CH₃.

The formed CH₃ radicals react further via two dominant pathways, namely by recombination with other CH₃ radicals into either C₂H₆ (45 %) or C₂H₄ (23 %) with the formation of H₂. The latter reaction occurs somewhat later during the pulse (see below).

These recombination reactions occur within the plasma, but a fraction of the CH_3 radicals also leaves the plasma and recombines to C_2H_6 in the cold surrounding zone (25 %). The position where the radicals recombine is important, as the gas temperature within the plasma is still rising. When the gas temperature has increased to ca. 2100 K, C_2H_6 is also subject to thermal decomposition into CH_3 (25 %). However, the majority of C_2H_6 (59 %) leaves the plasma towards the cold zone, where it is stable. Finally, the H atoms that diffuse to the cold zone (shown with an arrow denoting “Diff. from plasma”, and % represents the destruction rate, like for the other species) either recombine with CH_3 , also found in the cold zone (20 %), or react further with cold CH_4 , forming again CH_3 , as well as H_2 molecules (80 %).

After pulse initiation, hence during later stages of the pulse, when a high gas temperature is reached, the chemistry shifts. The dominant ion shifts from CH_3^+ and CH_4^+ to C_2H_5^+ . In addition, both CH_3 and C_2H_6 undergo several reactions leading to C_2H_5 . Furthermore, CH_3 has a direct pathway to C_2H_4 (23 %), as explained above, and almost all C_2H_5 (99 %) is also converted to C_2H_4 within the plasma, via H abstraction by any neutral molecule. The small fraction of C_2H_5 that moves towards the cold zone (1 %) also further reacts into C_2H_4 . Overall, most C_2H_4 is formed in the plasma and moves into the cold zone (92 %), resulting in the high C_2H_4 selectivity observed in our model. Finally, a small amount of C_2H_4 (8 %) reacts further into C_2H_3 and then C_2H_2 . As this step is thermal, it is highly dependent on the gas temperature; underestimating the plasma core gas temperature will result in overestimating C_2H_6 and C_2H_4 selectivities. The discrepancy with the experimental selectivities indeed suggests that our calculated plasma core gas temperature is slightly underestimated.

Near the end of the pulse, C_2H_5^+ recombines with electrons to either C_2H_3 and two H atoms (60 %) or C_2H_4 and one H atom (40 %). Finally, in the afterglow, C_2H_3 reacts further into C_2H_2 upon H abstraction (90 % within the plasma). Thermal reactions can still occur within the plasma if the gas temperature is high enough, but this is limited under condition B. Hence, all C_2H_2 will diffuse towards the cold surrounding zone, as well as a fraction (10 %) of the C_2H_3 , which will either react in the cold zone to C_2H_2 (71 %) or to C_2H_4 (29 %).

Figure 6-6 illustrates the reaction pathway analysis for condition E, in both the plasma and cold zones. We will mainly emphasize the difference between Figure 6-6 and Figure 6-5, as many of the reaction pathways are very similar for both pulse conditions. Two

key differences here are the elevated gas temperature (calculated to reach 3400 K, vs 2200 K for condition B) and the longer power-density deposition (see Figure 6-2).

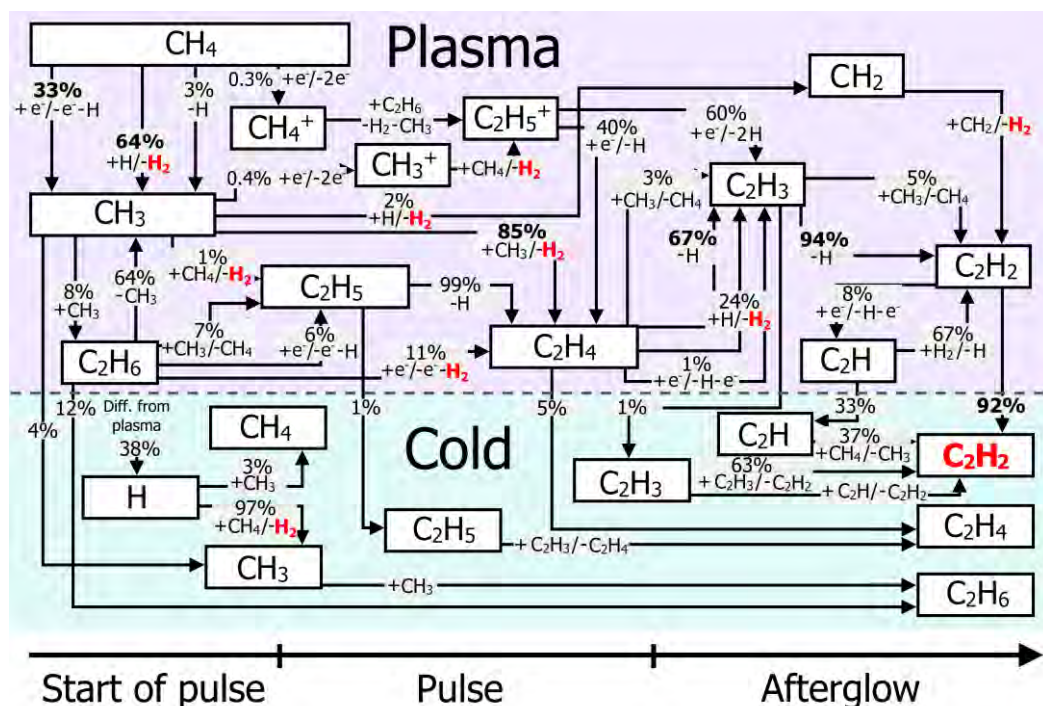


Figure 6-6 - Chemical reaction pathway analysis for condition E, showing the conversion of one species to another in both the plasma and cold zone. For each reaction, the co-reactant and co-product are indicated on the reaction arrow, together with the relative contribution of that reaction to the overall destruction of the considered species. If no percentage is present (a single arrow), this reaction denotes 100 % of the species destruction. Reactions with relative contributions below 1 % are omitted, except for the initial ionization reactions to show the dominant ions. The major pathway is indicated with the relative contribution (%) shown in bold, leading to the major products shown in bold and red. H₂ as a co-product is indicated in bold, red font each time.

First, the higher gas temperature makes that CH₄ splitting with any neutral reacting species become non-negligible (3 %). Furthermore, the chemistry involving CH₃ and C₂H₆ shifts significantly. CH₃ recombination to C₂H₆ is no longer the dominant pathway, as the production of C₂H₄ becomes much more important (from 23 % in Figure 6-5 to 85 % in Figure 6-6). In addition, C₂H₆ now mainly dissociates back into CH₃ (64 %; this occurs later in the pulse, but is shown here in the figure, for visual clarity), and only a limited fraction (12 %) moves towards the cold zone. This explains the low C₂H₆ selectivity at longer pulse durations. Finally, the longer pulse duration allows for high-energy electrons to be present after C₂H₆ is formed, leading to electron-impact dissociation of C₂H₆ towards

C₂H₄ (11 %). The ions, on the other hand, follow the same pathways as for condition B, as their chemistry is electron-impact driven.

During the pulse, rapid thermal chemistry shifts the product composition. C₂H₄ transport towards the cold zone is no longer dominant. Instead, three thermal reactions, as well as one electron-impact reaction (sum 95 %), yield the formation of C₂H₃, which thermally decomposes to C₂H₂. The high-energy electrons still present at the end of the pulse react with the large fraction of C₂H₂ in the plasma, forming C₂H (8 %). Eventually, thermal reactions in either the plasma or cold zone will result in the formation of C₂H₂ again.

Due to complete CH₄ dissociation, as discussed with Figure 6-2, a lot more H atoms are available in the plasma zone in condition E. This leads to a large increase in H atom movement from the plasma zone to the cold zone, from 1 % for condition B to 38 % for condition E. This “instant transport” of reactive H atoms to the cold zone is, however, an approximation of our global model. In reality, these H atoms would react near the plasma edge. The same approximation also explains the lower C₂H₄ selectivity in our model compared with experiment for the longer pulse group, as shown in Figure 6-3. Indeed, our model predicts that the C₂H₄ formed in the hot plasma zone is almost completely desaturated towards C₂H₂. This is an overestimation compared to the experiment, because there is no intermediate temperature zone in the model, where C₂H₄ can remain stable.

We note two important differences with Figure 6-5, related to C₂H formation. First, extending the pulse to a duration where electron-impact reactions break C₂H₂ will only shift selectivity further towards C₂H₂, as C₂H has no pathways to other hydrocarbons. This is also observed in our experiments [124], where the pulse duration was extended to 500 ns. Second, following the Kassel mechanism, C₂H is a very good precursor for solid carbon deposits [235,236]. This is also in line with our experiments, where high pulse frequencies (2000 Hz) could not be combined with long pulse durations (> 100 ns) due to excessive carbon deposits [124], which cannot be captured by our global model.

Overall, Figure 6-5 and Figure 6-6 explain why at shorter pulse durations our model mainly predicts C₂H₆ and C₂H₄ formation, with limited fractions of C₂H₂, while at longer pulse durations mainly C₂H₂ formation is predicted, with limited fractions of C₂H₄ and C₂H₆. Although the differences in our calculated product selectivities between conditions B and E are more pronounced than in our experiments, probably due to a slight underestimation of the calculated core plasma gas temperature for condition B, the

above reaction pathway analysis can still qualitatively explain the selectivity trends observed in our experiments.

6.3.4 Suggested improvements based on modeling insights

Comparing Figure 6-5 and Figure 6-6 shows the intricate interplay between thermal chemistry and electron-impact chemistry. The electron-impact reactions not only act as an initiator for CH₄ decomposition, but also play a significant role in further dehydrogenation of hydrocarbons at longer pulse durations (where the electrons have a longer lifetime). As C₂H₄ is the hydrocarbon with the highest market value (600 – 1200 \$/ton, depending on the region [237], with 225 million tons produced per year [238], while C₂H₆ is mostly a feedstock for C₂H₄ [239], and C₂H₂ is mainly used for vinyl chloride monomer production [240]), a simple follow-up question arises: can we use our modeling insights to improve the selectivity towards C₂H₄? We believe we can further tune the selectivity by means of the gas temperature, and therefore, we study here the effect of gas preheating on the product selectivity, and also on the EC.

Figure 6-7 presents the calculated C₂H₆, C₂H₄, and C₂H₂ selectivities for all pulse conditions, with different starting gas temperatures (300, 500, 700, and 900 K). The power density profile for the various pulse conditions is the same as in Figure 6-2.

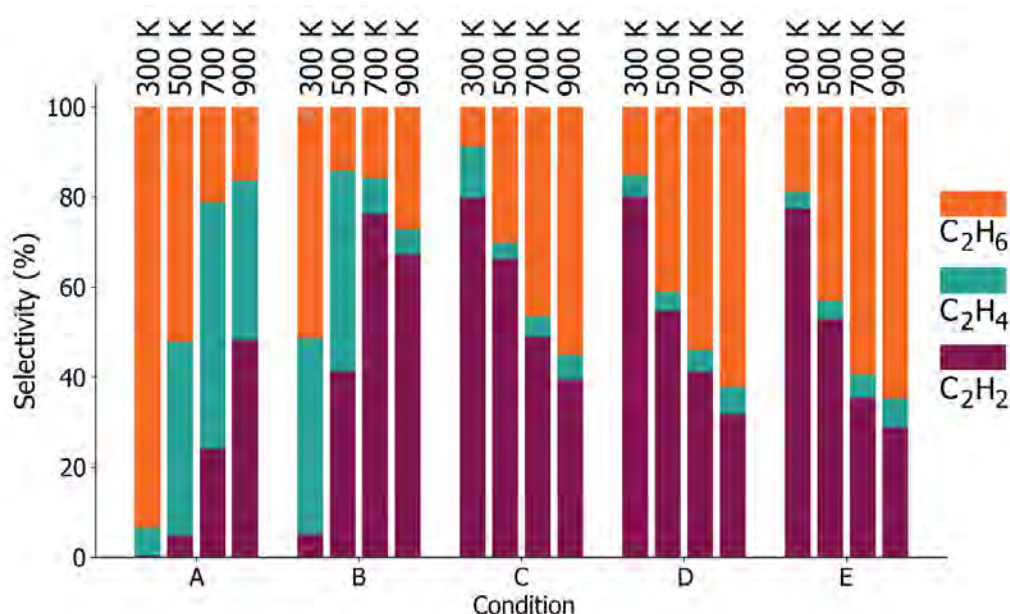


Figure 6-7 - Calculated C₂H₆, C₂H₄, and C₂H₂ selectivities for all pulse conditions, with different starting gas temperatures (300, 500, 700, 900 K).

We can observe two opposing trends in Figure 6-7. First, a higher initial gas temperature for condition A is beneficial for the selectivity of C_2H_4 and C_2H_2 . This is to be expected and in line with the discussion on the thermal reactions in Figure 6-5 and Figure 6-6. Indeed, a higher temperature typically leads to more C_2H_4 and C_2H_2 [71,125,209].

On the other hand, preheating above 700 K for condition B, or any preheating for longer pulse durations, suggests an increase in C_2H_6 selectivity. This seems very counterintuitive and in contradiction to the results for condition A. However, this is attributed to the pressure effect. Indeed, while the initial gas temperature changes, the initial pressure stays 1 atm. This means that the gas density, at 900 K for instance, is three times lower. This also means that the deposited power is heating less gas, and the gas temperatures can reach much higher values.

In the case of condition E and 900 K pre-heating, for instance, the gas temperature reaches 7100 K, leading to complete dissociation of CH_4 into C and H atoms. Subsequently, a large fraction of the H atoms moves towards the cold zone, where they react with CH_4 . As shown in Figure 6-5 and Figure 6-6, this results in CH_3 formation, leading to direct recombination into C_2H_6 .

Indeed, in the case of condition E, for instance, our model predicts a very limited fraction of C_2H_6 formation in the plasma, but more pronounced C_2H_6 formation in the cold region. The main product within the plasma at this condition is, however, still C_2H_2 .

To our knowledge, the effect of gas preheating has not yet been investigated in ns-pulsed plasmas. Therefore, we cannot experimentally verify the above model predictions. We understand from our experimental validation that our model somewhat exaggerates the selectivity trends, and thus, the increase in C_2H_6 selectivity upon preheating at longer pulse durations will likely be less pronounced than predicted above, if significant at all. However, our model does suggest that gas preheating to eliminate all saturated hydrocarbons for long pulse durations would not be a valid pathway, as cold CH_3 radicals near the plasma edge will always recombine to some extent into C_2H_6 . The only way to fully ensure no C_2H_6 formation by gas preheating would be to already heat the gas above the thermodynamically favorable temperature for C_2H_6 , which is essentially just thermal CH_4 pyrolysis [209]. Other avenues of suppressing C_2H_6 formation should be the subject of future research.

Overall, we find preheating to be beneficial for short pulse durations, i.e., condition A, and limited preheating for condition B. Combining short pulse durations with preheating

could thus be of great benefit to enhance both C₂H₄ and C₂H₂ production. In addition, post-plasma catalysis could promote C₂H₂ hydrogenation towards C₂H₄ [217].

Finally, because EC is also an important criterion for industrial potential, besides product selectivities, we present in Figure 6-8 the calculated EC values for all pulse conditions, with different starting gas temperatures (300, 500, 700, 900 K). We define the EC (kJ.mol⁻¹) as the energy needed to convert 1 mol of CH₄:

$$EC = \frac{\int_{t_{start}}^{t_{end}} P_d(t) V_p dt}{n_{CH_4_{start}} - n_{CH_4_{end}}} \quad [96]$$

Here, t_{start} and t_{end} are the start and end times of the simulation (s), $P_d(t)$ is the input power density profile as a function of time (W.m⁻³), and V_p is the plasma volume (m³), which is constant, as explained above.

Note that the additional energy needed to preheat the CH₄ is only considered for the converted CH₄ fraction. Indeed, energy in preheated, unconverted CH₄ is not considered to be lost. This makes sure that the EC predicted by our model is independent of the size of the cold zone.

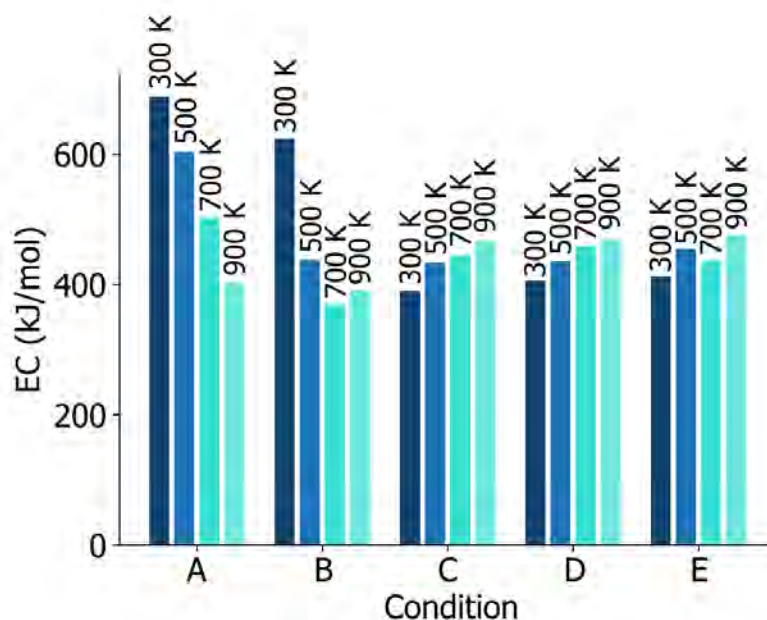


Figure 6-8 - Calculated EC per CH₄ converted for all pulse conditions, with different starting gas temperatures (300, 500, 700, 900 K).

The lowest EC predicted by our model without preheating (i.e., starting at 300 K) is ca. 400 kJ.mol⁻¹, for the long pulse group. This value agrees well with experimental results for ns-pulse CH₄ conversion from the literature, as Van Rompaey et al. [71] obtained an EC of 460 kJ.mol⁻¹, Delikonstantis et al. [217] achieved a lowest EC of 382 kJ.mol⁻¹, and both Lotfalipour et al. [222] and Scapinello et al. [236] reported ECs between 450 and 500 kJ.mol⁻¹. Note that this value of 400 kJ.mol⁻¹ CH₄ converted is only half of the target value that we claimed in the Introduction for plasma-based CH₄ conversion to be competitive with SMR. However, this target value applies to the simultaneous production of pure C₂H₄ and H₂, without other hydrocarbon products, while Figure 6-3 clearly shows that we do not produce pure C₂H₄ and H₂, but a mixture of all C₂ hydrocarbons, and the required separation costs would further increase the overall EC. Hence, we need to conclude that our plasma process is not yet competitive with industrial SMR [72,157,220,221].

Without preheating (300 K), our model predicts a clear drop in EC from the short pulse group towards a constant EC at the long pulse group. This higher EC at the shortest pulse durations is due to undesired CH₃ and H recombination into CH₄ in the cold zone (see section 6.3.3).

Regarding the effect of preheating, we again observe two opposing trends in Figure 6-8. First, we see a drop in EC upon preheating for condition A, as well as for condition B, up to 700 K. Indeed, the more pronounced thermal chemistry allows for optimal use of the radicals and minimizes the amount of recombination to CH₄. However, as soon as radicals do not recombine into CH₄ anymore, but all radicals form C₂H₆, C₂H₄, C₂H₂, or H₂, which occurs at longer pulse durations, any additional energy input (by preheating) is just wasted as gas heating. The latter explains the increasing trend in EC upon preheating for longer pulse durations.

Our model predicts that the minimum EC (namely 370 kJ.mol⁻¹ CH₄ converted) is reached at condition B with an initial gas temperature of 700 K. This value is close to the 382 kJ.mol⁻¹, reported by Delikonstantis et al. [217]. On the other hand, preheating to only 500 K yields only slightly higher EC (440 kJ.mol⁻¹), and a more favorable product selectivity (i.e., 45 % towards C₂H₄; cf. Figure 6-7), while preheating to 900 K for condition A also yields only a slightly higher EC of 400 kJ.mol⁻¹, and also a higher selectivity towards C₂H₄ (i.e., 36 %; cf. Figure 6-7). Overall, our model predicts that preheating with short pulse durations is very promising, as it enables more valuable product compositions while keeping EC relatively low.

6.4 Conclusion

In this work, we studied the effect of pulse energy (or pulse duration) on CH₄ conversion into C₂ hydrocarbons and H₂ in ns-pulsed plasma, using a two-zone global modeling approach, allowing us to solve the heat balance equation and energy and mass exchange between the hot plasma zone in the center and the colder surrounding zone. Our model reveals a higher gas temperature upon longer pulse duration, up to 3500 K. Furthermore, it predicts a large pressure peak in the early stages of the pulse, ranging from 4.9 bar for condition A, up to 15.3 bar for condition E. This high-pressure peak is, however, very short-lived and only lasts a few 100 ns. Furthermore, a longer pulse duration yields a significant shift in product selectivity, promoting unsaturated hydrocarbons.

To understand this shift in product selectivity, we analyzed the chemical reaction pathways for a short (condition B) and longer (condition E) pulse. Our analysis shows that low gas temperatures, for condition B, promote CH₃ radical recombination towards C₂H₆ (and to a smaller extent also C₂H₄), explaining their high selectivities predicted by our model, and also found experimentally. Increasing the pulse duration to the long pulse group (> 30 ns FWHM) not only shifts the selectivity to C₂H₂ via thermal reactions, but electron-impact reactions also contribute significantly towards dehydrogenating the

hydrocarbons, leading to high C_2H_2 selectivity, as predicted by our model, and confirmed by our experiments. However, it also leads to the electron-impact reaction with C_2H_2 , which is important for the formation of C_2H , a known precursor for soot formation.

Finally, we used our modeling insights to target improved C_2H_4 selectivity. Although our model reveals that avoiding all C_2H_6 formation is impossible, it also demonstrates that gas preheating at short pulse durations (< 30 ns) can be a viable strategy for shifting selectivities towards C_2H_4 (and C_2H_2) at low EC. In future work, we want to further explore this strategy by verifying our global model predictions with multidimensional modeling of CH_4 ns-pulsed plasmas, as well as through experiments. Overall, we believe that ns-pulsed plasmas are promising for CH_4 conversion to H_2 and C_2 hydrocarbons, with a primary focus on C_2H_4 , by carefully tuning the pulse duration in combination with gas preheating.

Chapter 7

Understanding soot formation in a rotating gliding arc plasma via multidimensional modeling

The content of this chapter is in part based on:

Controlling solid carbon formation in gliding arc CH₄ plasmas

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In this chapter, we present a computational fluid dynamics model to elucidate the underlying flow dynamics and their effect on soot formation. Our results show that CH_4 conversion strongly depends on flow rate, as validated by experiments, whereas product distribution remains unaffected by gas flow rate. Modeling indicates that carbon formation primarily proceeds via the polycyclic aromatic hydrocarbon (PAH) mechanism, linking carbon atoms into graphene-like sheets. Our work provides mechanistic insight into carbon formation in CH_4 gliding arc plasmas and allows for future predictive modeling of CH_4 plasmas.

7.1 Introduction

It is clear that CH_4 plasmas do not only produce H_2 and hydrocarbons, but also solid carbon. While the latter can be of high value (e.g., carbon black, carbon nanotubes, graphene...), producing solid carbon with the desired characteristics is quite challenging. Most often, solid carbon deposits, or soot formation, is detrimental for the experiments, as it makes the plasma unstable and even lead to plasma extinguishing. We observed this in the experiments of Chapter 3 and Chapter 6, and it is also often reported in the literature [217,228,235,241,242].

Until now, we have avoided modeling soot (i.e., any type of solid carbon) formation due to its extremely complex chemistry and the multiple phases that must be accounted for. However, in this chapter, we present our first efforts of modeling soot formation, by describing the precursors that ultimately form soot. We developed this model to better understand the experiments performed by another PhD student, Callie Ndayirinde, within PLASMANT, who studied various methods to avoid soot formation. Therefore, this chapter can help pave the way for future reactor design via modeling, by adjusting gas flow dynamics to actively suppress soot formation.

7.2 Computational details

We simulate the experiments by Callie Ndayirinde, using a 2D axisymmetric CFD model, to gain better insight into product selectivities and solid carbon formation. To accurately capture the chemistry, we need a relatively large chemistry set of 43 species. While computationally demanding, it can be solved in a coupled manner with a few reasonable approximations. In essence, our model follows the same approach used previously for smaller chemistry sets, such as air plasma or plasma-based CO_2 conversion [194–197]. The full details of the modeling method, including chemistry set reduction, can be found in Chapter 2. The performance metrics, such as conversion and selectivity, are calculated using the equations in Chapter 3. In this chapter, we only present the aspects that are different from our previous CFD models.

7.2.1 Major mixture-averaged diffusion

When dealing with 43 species, the most computationally demanding part of the model is the transport equation. We therefore propose a reduced description of the transport equation based on major mixture-averaged diffusion. Let's consider the diffusive flux vector from the Maxwell-Stefan diffusion model, as shown in Chapter 2:

$$\mathbf{j}_i = -\left(\rho D_i^m \nabla w_i + \rho w_i D_i^m \frac{\nabla M_n}{M_n} - \mathbf{j}_{c,i} - \mathbf{j}_{T,i}\right) \quad [97]$$

The description of D_i^m loops over all binary diffusion coefficients twice via:

$$D_i^m = \frac{1 - w_i}{\sum_{k \neq i} \frac{x_k}{D_{i,k}}} \quad [98]$$

In the major mixture-averaged approach, each species diffuses into only the major components present in the gas mixture. D_i^m is therefore calculated for each species in the gas mixture comprised of Ar, C, H, H₂, CH₄, and C₂H₂, denoted as species k in equation 98.

We use this approximation only for calculating D_i^m and not for other variables. This approximation to the transport of species allows us to solve the Maxwell-Stefan diffusion model on a more refined mesh, thus enabling more accurate results. All thermodynamic and transport properties are calculated based on the species-specific NASA polynomials and transport data [55,243,244]. The complete expressions used to obtain the mixture properties from the individual species properties are provided in Chapter 2. This section also describes the calculation of the electrical conductivity.

7.2.2 Geometry and boundary conditions

We model here the RGA plasma reactor; see schematic of the geometry in Figure 7-1. Like the other plasma reactors studied in this thesis, it can also be approximated as 2D axisymmetric.

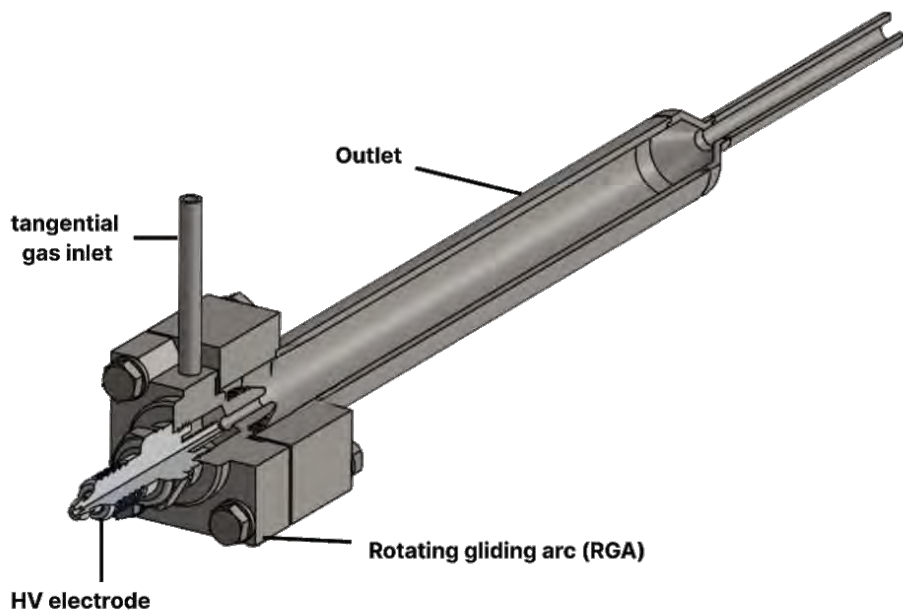
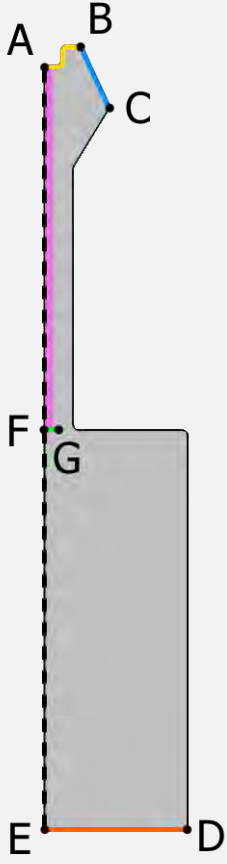


Figure 7-1 - Schematic representation of the rotating gliding arc plasma reactor.

The boundary conditions for our 2D axisymmetric model, as well as a schematic of the geometry in the model, with indication of the boundaries, are presented in Table 7-1 [108,110,113,120,121].

Table 7-1 - Boundary conditions for the 2D axisymmetric model. The gas inlet (BC) is indicated in blue, the high-voltage electrode (AB) in yellow, the virtual ground (FG) in green, the gas outlet (DE) in orange, and the plasma column (AF) in purple [108,110,113,120,121].

Geometry	Boundary	Flow	Heat transfer and current conservation	Transport of species
	High-voltage electrode (yellow) AB	$\mathbf{u} = \mathbf{0}$	$\int \mathbf{J} \cdot \mathbf{n} dS = I_0$ $-\mathbf{n} \cdot \mathbf{q} = \mathbf{0}$	$-\mathbf{n} \cdot \mathbf{j}_i = \mathbf{0}$
	Gas inlet (blue) BC	$\mathbf{u} = \mathbf{u}_0$	$\mathbf{J} \cdot \mathbf{n} = 0$ $T = 293.15 \text{ K}$	$w_i = w_{0,i}$
	Reactor wall (no color) CD	$\mathbf{u} = \mathbf{0}$	$\mathbf{J} \cdot \mathbf{n} = 0$ $-\mathbf{n} \cdot \mathbf{q} = s_e \sigma_{S-B} (T_{amb}^4 - T^4)$	$-\mathbf{n} \cdot \mathbf{j}_i = \mathbf{0}$
	Gas outlet (orange) DE	$[-p\mathbf{I} + \mathbf{K}]\mathbf{n} = -p_0\mathbf{n}$ $p_0 = 0$	$\mathbf{J} \cdot \mathbf{n} = 0$ $-\mathbf{n} \cdot \mathbf{q} = 0$	$-\mathbf{n} \cdot \rho D_i^m \nabla w_i = 0$
	Virtual ground (green) FG	/	$V = 0$	/

In Table 7-1, $\mathbf{u}_0$ is the imposed velocity field, taken from a 3D CFD (gas flow only) model at 4 SLM, following the method of Chapter 3 and Chapter 5, p_0 is the outlet pressure, set to 1 atm, $\mathbf{K}$ is the viscous stress tensor, $\mathbf{q}$ is the conductive heat loss, T_{amb} is ambient (room) temperature, s_e is the surface emissivity, set at 0.75, σ_{S-B} is the Stefan-Boltzmann constant, $w_{0,i}$ is the initial weight fraction, being 0.043 for CH_4 , 0.957 for Ar

(which corresponds to a molar fraction of 10 % CH₄ and 90 % Ar, as used in the experiments) and it is 0 for all other species, ρ is the gas density, D_i^m is the molecular diffusion coefficient, and I_0 is the user-defined total current flowing through the cathode, allowing for the required power to be deposited.

Due to the axisymmetric approach of our model, the grounded reactor wall (between point C and D) cannot be defined as the electrical ground in the model, as this would create a cone-shaped plasma when revolving in 3D, while in reality, the plasma is located in the center (see purple, between AF, in Table 7-1). Therefore, we define a virtual ground (FG) to ensure the plasma is located fully on the symmetry axis. Previous work on plasma-based NH₃ cracking has shown that the virtual ground approximation is valid within the SEI range considered in this study, as confirmed by the good agreement with experiments of Fedirchuk et al. [152] in the complementary study of Maerivoet et al. [245]. Although this was for another gas, the plasma characteristics are similar, due to the quasi-thermal character of the conversion process and similar flow dynamics. Physically, this implies that the plasma arc in the experiment must reach at least the virtual ground potential assumed in the model, which is the case, as confirmed by our experiments, i.e., interaction of the arc with the reactor walls, demonstrated by the localized damage to the stainless steel. Previous models comparing the solution of the current conservation equation set with an equivalent volumetric heat source have demonstrated that solving the current distribution results in a narrow and contracted plasma region [202]. Therefore, although the plasma can be represented as a thermal energy source, it acts as a highly localized spatial heater. This highlights the importance of considering the multidimensional nature of the plasma reactor, as opposed to representing the plasma as a homogeneous system.

The model is implemented within the COMSOL Multiphysics 6.3 framework and solved using a fully coupled (monolithic) approach, in which all dependent variables are assembled and solved simultaneously within a single global nonlinear system. Consequently, the coupling between the different physical fields, including the pressure–velocity interaction, is inherently accounted for through the Jacobian matrix, eliminating the need for separate pressure–velocity coupling algorithms such as SIMPLE or PISO. The governing equations are solved in their stationary form, as described below and in Supporting Information. The nonlinear solver iterations are considered converged when the relative tolerance of the solution is below 0.001, ensuring sufficient accuracy while maintaining computational feasibility.

A computational mesh consisting of approximately 30,000 triangular elements was generated to provide an appropriate balance between spatial resolution and computational cost. Due to the large number of elements, all variables were linearly discretised including a P1+P1 discretization for the flow and pressure. Particular attention was given to resolving regions with strong gradients, such as areas with significant variations in temperature, species concentration, and electromagnetic fields. The final mesh exhibits an average element quality of 0.925 and a minimum element quality of 0.550, indicating a high-quality discretization with no severely distorted elements. The selected mesh resolution was determined based on a systematic mesh convergence study, in which further mesh refinement resulted in negligible changes in the calculated quantities of interest.

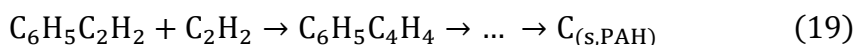
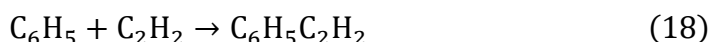
7.2.3 Chemistry set

Solid carbon formation in CH₄ plasmas is reported to occur via either the Kassel or PAH mechanism. In the Kassel mechanism, solid carbon is formed through sequential dehydrogenation steps [223,235], where M is any neutral gas species:

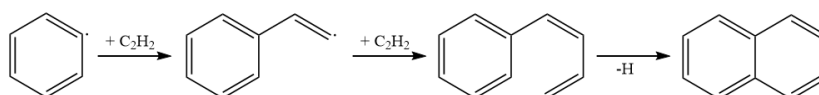


In the PAH mechanism, C₂H₂ is not dehydrogenated but undergoes further reaction to benzene (C₆H₆) via trimerization of C₂H₂ (reaction 9), via C₄H_x formation (reactions 10–15) or via propargyl (C₃H₃) recombination (reaction 16). Once the first ring (C₆H₆) is formed, PAHs grow via repetitive hydrogen abstraction, yielding C₆H₅ (the simplest aryl), followed by C₂H₂ addition (several hydrogen abstraction carbon addition steps, HACA) (abstraction as reaction 17 and addition as reaction 18), ultimately forming solid carbon (reaction 19) [246–248]:





The HACA mechanism can also schematically be represented as follows:



Describing the chemistry of solid carbon formation requires an extensively tested set of kinetics. Our chemistry set is based on the validated CRECK chemistry set [55,243,244], but to make the fully coupled 2D axisymmetric model computationally feasible with chemistry included, the number of species and chemical reactions is reduced following the method of Chapter 2. This results in a chemistry set comprising 43 species and 258 reactions from a starting list of 452 species and 24041 reactions [55,243,244]. The reduced chemistry model was validated against full chemistry calculations. The full chemistry reduction algorithm, and more information on the accuracy of this reduction, is presented in Chapter 2. We can safely conclude that this chemistry reduction has negligible influence on the predicted CH_4 conversion and major product species. Table 7-2 lists all species included in the model. Their reactions and corresponding rate coefficients are all adopted from the CRECK chemistry set [55,243,244]. This chemistry set adequately describes PAH solid carbon formation via PAH precursors, towards various species, ranging from C_{10}H_x up to C_{18}H_x (see Table 7-2), which are taken as the final precursors for $\text{C}_{(s, \text{PAH})}$. All other C_{10+} species adopted from the original CRECK chemistry set were found to be negligible by our reduction algorithm. We also added three more species to this chemistry set, to represent the solid carbon formed via the

Kassel mechanism (C_2 and C_3 as intermediate compounds, and $C_{(s, \text{Kassel})}$ as Kassel solid carbon; see Table 7-2).

Table 7-2 - Species included in the 2D model

General species	Small species	ring-like PAH precursors	Kassel precursors
Ar, H, H ₂ , CH ₄ , CH ₃ , CH ₂ , CH, C ₂ H ₆ , C ₂ H ₅ , C ₂ H ₄ , C ₂ H ₃ , C ₂ H ₂ , C ₂ H, C ₃ H ₈ , C ₃ H ₄ (-yne), C ₃ H ₄ (-iene), C ₃ H ₃ , C ₃ H ₂ , C ₄ H ₆ , C ₄ H ₄ , C ₄ H ₃ , C ₄ H ₂ , C ₆ H ₅ (linear)	C ₆ H ₆ , C ₆ H ₅ , C ₅ H ₅ , C ₇ H ₇ , C ₇ H ₆ , C ₆ H ₅ C ₂ H, C ₆ H ₄ C ₂ H	C ₁₀ H ₈ , C ₁₀ H ₇ , C ₁₂ H ₈ , C ₁₂ H ₇ , C ₁₄ H ₉ , C ₁₆ H ₁₀ , C ₁₆ H ₉ , C ₁₈ H ₁₀ , C ₁₈ H ₉	C, C ₂ , C ₃ , C _(s, Kassel)

The present model does not explicitly include charged or electronically excited species. Instead, the plasma is represented as a heat source governed by the Ohmic current equations, with all deposited electrical energy instantaneously converted into gas heating. This approximation is supported by previous studies indicating that electron-impact reactions and non-equilibrium effects become negligible at gas temperatures above ~2000 K for various gases, including CH₄-based plasmas [48,171]. In our plasma reactor, the plasma temperature is certainly above 2000 K. Additionally, the vibrational–translational relaxation of CH₄ is rapid, within timescales on the order of 70 μs at similar conditions, facilitating efficient thermalization [53]. This approach has been validated against experimental data in various plasma reactors and gas mixtures, demonstrating that purely thermal models can accurately reproduce experimental observations in warm plasmas, and indicating that non-equilibrium effects indeed play a minor role in determining overall reactor performance. However, it may still limit the accuracy of predicted quantities that are sensitive to local non-equilibrium effects, such as the core plasma temperature or electron properties [138,194,196,202].

7.3 Results and discussion

After validating the model by comparing conversion and selectivities, we aim to understand the process by comparing two flow rates. Finally, we aim to differentiate

between PAH and Kassel soot formation by linking each mechanism to a specific location in the plasma.

7.3.1 Model validation

First, we compare the calculated CH₄ conversion and product selectivities to the experimental results as model validation; see Figure 7-2, for a plasma power of 50 W and a gas flow rate of 2 L/min and 4 L/min. For the experimental methods, we refer to the paper this chapter is based on [249].

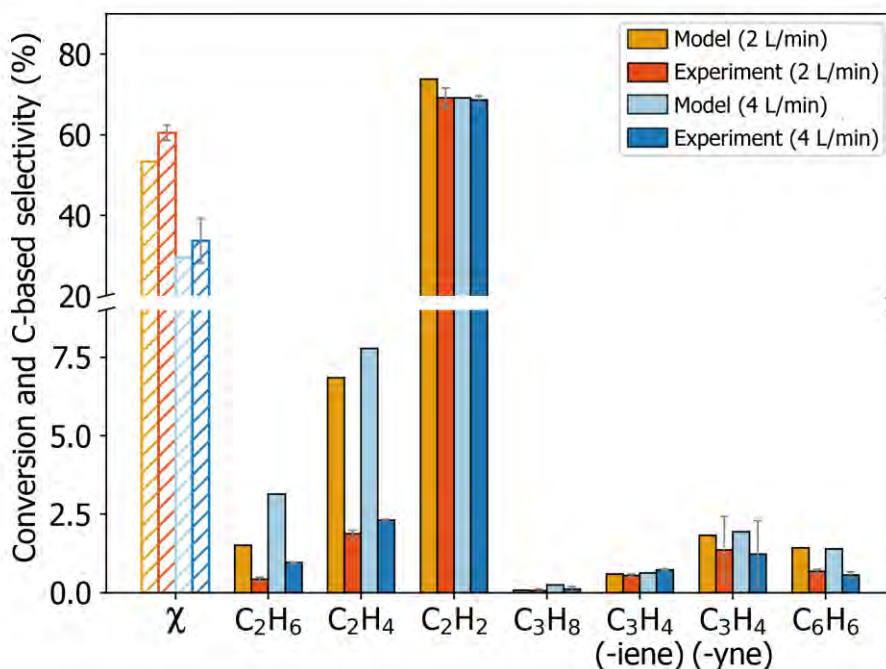


Figure 7-2 - Calculated and experimental CH₄ conversion and product selectivities for a plasma power of 50 W at 2 L/min and 4 L/min, with a 10/90 CH₄/Ar gas mixture.

The calculated and experimental trends of CH₄ conversion and hydrocarbon selectivities are in reasonable agreement, given the complexity of the chemical pathways. The conversion corresponds well between experiments and the model for both flow rates, i.e., 60 % and 53 % for 2 L/min, and 34 % and 30 % for 4 L/min, respectively. Comparing the C₂ hydrocarbon selectivities, we see the same increasing trend from C₂H₆ to C₂H₄ and further to C₂H₂, despite the overestimation of C₂ hydrocarbon selectivities in the model. This leads to a discrepancy between the sum of all selectivities in the model and in the experiment, as evidenced by the somewhat underestimated solid carbon formation

predicted by the model. This likely results from the fact that the plasma is more stable in the model than in the experiments, due to the axisymmetric modeling approach, i.e., by applying a “virtual ground” at the symmetry axis, as explained in section 7.2.2 above. Modeling the rotation of the plasma in 3D may lead to better agreement, but this is currently not feasible computationally, with the entire chemistry set included. However, the slight increase in desaturated C_2 hydrocarbon selectivities upon increasing flow rate, observed in the experiments, is also predicted by the model.

Both the experiment and the model see a negligible formation of C_3H_8 and the same increasing trend in product selectivity from C_3H_8 to C_3H_4 (-iene), with a significant fraction of C_3H_4 (-yne) produced in both experiments and the model. Finally, C_6H_6 selectivity is lower than C_3H_4 (-yne) in both the model and experiments, which strongly indicates that the model can provide a realistic picture of the kinetic formation of C_6H_6 , as C_6H_6 is a more thermodynamically stable product than C_3H_4 (-yne).

7.3.2 Changes in flow dynamics

As the model shows reasonable agreement with measured CH_4 conversion and product selectivities, it can be used to describe differences in flow dynamics and their effects on the plasma. Figure 7-3 compares the calculated gas flow and temperature profiles at 2 and 4 L/min.

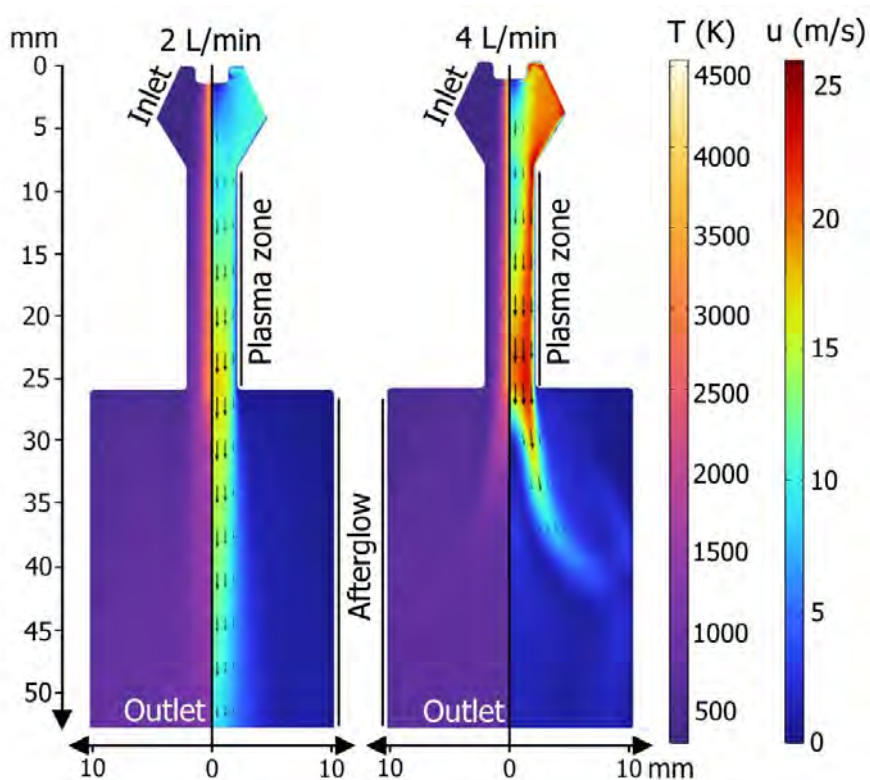


Figure 7-3 - Calculated temperature (left panels) and flow velocity profile (right panels) at 2 and 4 L/min. For the geometry, we refer to Table 7-1 in section 7.2.2 above.

The calculated velocity plots illustrate vastly different flow dynamics for 2 and 4 L/min. The 2 L/min gas flow velocity profile shows very limited cold gas flow at the wall in the plasma zone, from 10 to 25 mm, vertically, with velocities only around 17 m/s. In the afterglow, it exhibits jet-like behavior, as is also observable in the temperature plot, where the hot gas is pulled downstream. In contrast, the 4 L/min velocity profile exhibits a thicker cold gas layer in the plasma zone, evident from the high flow rates of around 22 m/s near the walls. The afterglow also behaves differently: a higher azimuthal velocity generates a stronger centrifugal force that, as the chamber volume increases, pushes the gas radially outward. This results in a tornado-like shape with a center of diminished gas velocity, as observed in the flow profile. As a result, there is faster mixing and quenching of the gas, resulting in faster cooling of part of the arc that escapes from the plasma reactor and enters in the expanded afterglow chamber which attaches to the actual ground in the experiment [250]. This ultimately leads to the higher current and voltage fluctuations observed experimentally at higher flow rates [249].

These differences suggest there is a large difference in the ratio of azimuthal to axial flow between both flow rates, i.e., the ratio of the flow components near the virtual ground is ~ 0.4 and ~ 0.8 for 2 L/min and 4 L/min, respectively. This is expected because although the flow rate doubles, the gas temperature does not; therefore, the gas dynamics are sensitive to changes in the dominant velocity component. The gas temperature, however, increases with flow rate, reaching 4600 K at 4 L/min compared to 3500 K at 2 L/min. The validity of this calculated temperature at the centre of the arc cannot be verified, as the temperature cannot be measured in this reactor. Therefore, we do not make any strong claims about the actual temperature in the centre, resulting from our conductivity approximation. However, we have extensively verified that a change in the arc temperature does not significantly alter the conversion and product selectivities, as long as the deposited power remains constant, and therefore, even if the actual temperature would vary (even up to ± 400 K), this would not affect our calculated conversion and product selectivities. More information can be found in the work by Quiroz Marnef et al. [202].

7.3.3 Localization of soot formation

The overall impact of gas flow dynamics on soot formation can be understood by plotting the major molar concentration profiles (in %) for the two mechanisms (PAH and Kassel precursors), calculated by our model; see Figure 7-4. Our model accounts for the additional reactions that C_6H_6 can undergo to produce PAH precursors, as presented in Table 7-2 above. The Kassel mechanism is accounted for by assuming that 50% of collisions between C_2 and C_3 in the plasma result in solid carbon formation. This value is taken from the sticking coefficient of C_3 on carbon surfaces [251]. Specifically, we plot in Figure 7-4 the calculated species concentration profiles of CH_4 , C_2H_2 (as the main product), C_6H_6 , PAH precursors, C_3 , and Kassel precursors (see Table 7-2), at a 2 L/min flow rate.

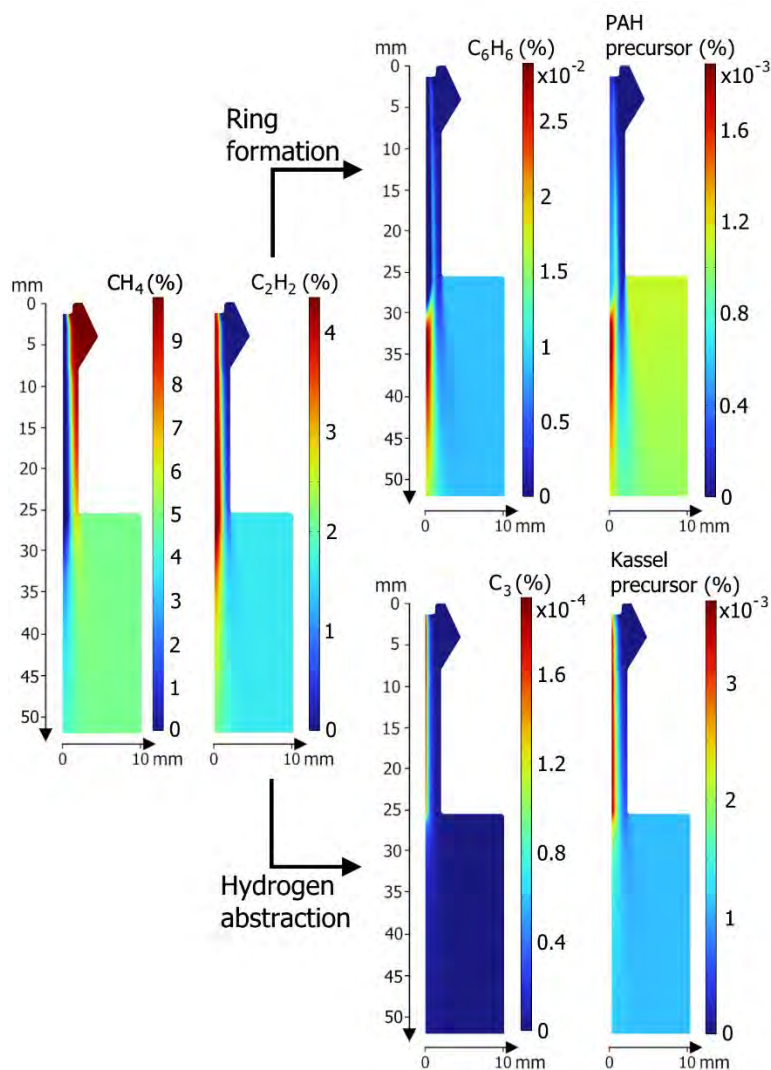


Figure 7-4 - Calculated species concentration profiles for CH₄, C₂H₂, C₆H₆, PAH precursors, C₃, and Kassel precursors, at 50 W and 2 L/min.

The figure distinguishes between the two pathways towards soot formation, both starting from C₂H₂. Indeed, either ring formation occurs to form C₆H₆, leading to various PAH precursors, or C₂H₂ undergoes additional H abstraction due to the high temperature and becomes C₃, resulting in Kassel precursors.

We can observe from Figure 7-4 that inside the plasma, CH₄ is mainly converted into C₂H₂, but the afterglow is very important for the formation of PAH precursors. Indeed,

the cold CH_4 mixing with the plasma afterglow allows for residence times long enough, in the range of a few milliseconds, to start the formation of aromatic compounds (C_6H_6 , C_7H_7 , $\text{C}_6\text{H}_5\text{C}_2\text{H}$, ...) that lead to PAH precursors [55,243,244]. This suggests that altering flow dynamics may suppress PAH solid carbon formation, which has indeed been observed experimentally by Biondo et al. [252].

In contrast to the PAH precursors, which are mainly formed in the afterglow, the Kassel precursor is solely formed inside the plasma (see Figure 7-4). Indeed, the Kassel mechanism requires dehydrogenated C_2 and C_3 species for solid carbon formation, which are present only at 2500 K and above [209]. Hence, all carbon filament formation in the plasma will be driven by soot formation following the Kassel mechanism.

Figure 7-5 presents the accumulated formation rates of both PAH and Kassel precursors as a function of distance from the high-voltage electrode, with the plasma and afterglow zones indicated. The sum of both curves at the end of the simulation domain (corresponding to the reactor outlet) is equal to 100%.

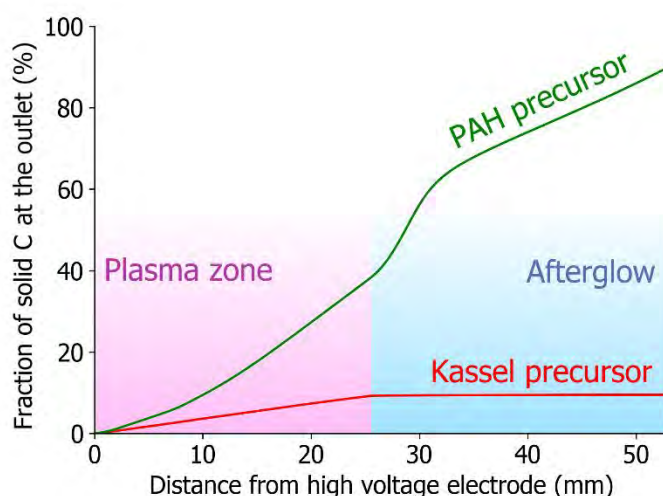


Figure 7-5 - Accumulated formation rates of solid carbon following the Kassel and PAH mechanism, as a function of distance from the high voltage electrode, at 2 L/min. The plasma zone and afterglow are indicated in purple and blue, respectively. Our model predicts 10 times more PAH soot formation compared to Kassel soot formation.

Our model predicts that the concentration of solid carbon at the reactor outlet formed via the PAH mechanism is 10 times larger than via the Kassel mechanism for a gas flow rate of 2 L/min (accumulated fraction roughly 90% for PAH precursors vs. ca 9% for

Kassel precursors). We can, however, not validate this model prediction because neither SEM, TEM, nor TGA can quantify the amount of solid carbon formed via either the PAH or Kassel mechanism. Furthermore, the kinetic data for the Kassel soot formation mechanism have not been verified and are therefore subject to unknown errors; additional kinetic data on this mechanism would be needed to validate this model.

Overall, we can however carefully conclude from our model that, although not the dominant mechanism, Kassel solid carbon formation is unavoidable in arc plasmas, as the core plasma temperature will always reach above 2500 K for warm plasmas. On the other hand, our model predicts that PAH precursors are more dominant at the conditions under study, but also that their formation can be affected by the cooling rate in the afterglow, thus possibly reducing or even avoiding their formation by means of flow dynamics. This will be investigated in our future work.

7.4 Conclusion

In this chapter, we presented a multidimensional model for CH_4 reforming to assess soot formation and the effect of gas flow dynamics. We found a significant shift in gas flow dynamics when increasing the flow rate from 2 to 4 L/min, with the flow transitioning from a jet-like afterglow to a tornado-like flow with a center of diminished velocity. The latter leads to experimental instabilities.

Furthermore, we found that PAHs form more soot at the edge of the plasma and in the afterglow, and not at all in the plasma core. Dehydrogenation of C_2H_2 , on the other hand, leads to soot formation in the plasma core. Hence, we can clearly identify the location of soot formation for each mechanism. While we predict PAH soot formation to be dominant over the Kassel mechanism (dehydrogenation), additional kinetic data on the latter are needed to support this claim.

In conclusion, we successfully developed a CH_4 model that can accurately predict experimental conversion and product selectivities. Although the mechanism of soot formation is described in a simple way, in future work, this model could be used for product optimization and soot suppression, in order to support experiments.

General conclusions and outlook

We presented various models in this thesis, for various plasma reactors and chemistries (DRM, NH_3 cracking and CH_4 conversion), all towards H_2 production. We applied different computational methods and made significant advancements in both multidimensional and global models, towards a higher degree of predictiveness. In this chapter, we provide general conclusions for each of the previous research chapters, explaining the main chemical or physical takeaways the model teaches us. In the second part of this chapter, we give a more personal outlook on the current and near-future state of plasma modeling.

8.1 Conclusions

The production of H_2 by warm and non-thermal plasma has been studied in detail by experimentalists. Yet, warm and non-thermal plasma chemistry and physics are still poorly understood. Models can provide a better understanding of the system, especially when they are built from scratch, using physical equations, and validated with experiments without tunable parameters. Such a predictive model can provide accurate insights into the underlying mechanisms. In this thesis, we developed several models with various degrees of predictability, to understand the chemical and physical mechanisms of various plasma systems.

In **Chapter 3**, we developed a model for an atmospheric pressure glow discharge (APGD) plasma, to assess changes in chemistry in DRM upon O_2 addition. We observed a large shift in chemistry due to the additional heating from O/O_2 reacting with CH_4 . This shift results in additional CH_4 conversion upon increasing O_2 fraction, as validated by experiments. Furthermore, our model predicts that the water-gas shift reaction is significant in the afterglow, shifting the product composition towards a higher syngas (H_2/CO) ratio. Finally, we demonstrated that both global models and local chemical equilibrium models are not suitable for modeling contracted atmospheric-pressure plasmas for DRM with O_2 addition, and we believe this conclusion is valid for any contracted atmospheric-pressure plasma with slow kinetics.

In **Chapter 4**, we developed a global NH_3 model, not to describe a single reactor but to scan over a wide range of gas and electron temperatures, for possible energy-efficient pathways for NH_3 cracking. We find that the lowest EC for continuously operating plasma systems is provided by the thermal pathway using a warm plasma, reaching an EC of around 200 kJ.mol^{-1} . Here, we define two chemical pathways for NH_3 cracking: one following dehydrogenation of NH_3 to NH , leading directly to N_2 . The second pathway in thermal NH_3 cracking involves N_2H_2 as an important intermediate, in both the cis and trans configurations. Finally, we propose a way to lower the EC, by preheating the gas before short nanosecond-range pulses, reaching an EC of 157 kJ.mol^{-1} , which we define as “plasma-initiated thermal NH_3 cracking”.

Chapter 5 explores the gas flow dynamics of NH_3 cracking by multidimensional modeling. First, our multidimensional model also predicts that both thermal pathways described in the previous chapter are important. Specifically, we use this multidimensional model to study the effects of turbulent transport on NH_3 cracking, and we find that turbulent transport effects are detrimental to NH_3 conversion, as turbulent heat transfer quenches

the afterglow, which would otherwise allow additional “free” conversion. This contrasts with CO₂ splitting and NO_x formation in warm plasmas, where rapid quenching in the afterglow is necessary to freeze the desired products chemically. Hence, we propose microwave plasmas and plasma jets, characterized by a long afterglow, as suitable plasma reactors for NH₃ cracking with warm plasma.

In **Chapter 6**, we developed a two-zone global model to improve the existing global models for nanosecond pulsed plasmas, which typically require gas temperature and pressure as input in the models. Our calculated gas temperature corresponds to temperature measurements reported in the literature. Our global ns-pulsed model predicts temperatures in the range of 2000 to 3000 K. Furthermore, reasonable agreement with experimental selectivities indicates that this model can provide insights into the underlying chemistry with minimal user input. We can explain the shift in selectivity from short (< 30 ns) to longer (> 30 ns) pulses based on the gas temperature within the plasma. Lower temperatures at shorter pulse durations allow more radical recombination, resulting in more saturated hydrocarbons, while higher gas temperatures at longer pulse durations promote further desaturation. Finally, we show that, also for CH₄ conversion, preheating might be a viable strategy to shift selectivities towards the more desirable C₂H₄ using shorter-duration pulses.

In **Chapter 7**, we developed a multidimensional model to assess soot formation in CH₄ arc plasmas. We suggest that soot formation can be subdivided into two mechanisms: via polycyclic aromatic hydrocarbons (PAHs) and via C₂H₂ dehydrogenation (Kassel mechanism). While the former occurs in the plasma edge and afterglow, the latter occurs solely in the plasma core. Our model reveals that the PAH mechanism is dominant over the Kassel mechanism, and therefore, future modeling could explore reactor designs that suppress soot formation via gas-flow dynamics.

8.2 Outlook

Predictive modeling can shed light on interesting mechanisms at play in warm plasma systems. The multidimensional models developed in this thesis, along with other multidimensional models developed in PLASMANT over the past few years [194–197,202], have shown good agreement with warm plasma experiments, based on solely describing thermal chemistry. Indeed, it appears that plasma chemical processes (such as electron-impact reactions, excited states, or ion chemistry) do not contribute to a significant extent to the chemistry in a warm plasma.

Thus, the question arises, if these warm plasmas can be described with thermal chemistry, what is the point of using a plasma? Why can we not just heat a gas mixture in a traditional reactor? In my opinion, the competitive edge of plasma technology for gas conversion is the physical edge of the plasma. We demonstrate in Chapters 3 and 5 that the main chemical reactions occur near the edges of the plasma core still away from the cold walls, where the gas enters a chemically active region with extremely high temperature gradients. For Chapter 3, for instance, these high gradients prevent the products (CO and H_2) from reacting (back) into CO_2 and H_2O . This edge can however also be detrimental, as Chapter 7 illustrates that it also drives much of the PAH soot formation in CH_4 arc plasmas. Even the two-zone model of Chapter 6 indicates that transport of radicals from the plasma zone to the cold zone results in unwanted saturated hydrocarbons in the cold zone, once again demonstrating the dominant role of the plasma edge for the eventual product composition.

Furthermore, the plasma is a non-solid heater, meaning that the extremely high temperatures are reached away from solid materials. With the correct gas flow dynamics, this allows for the high temperature chemistry to occur without damaging the reactor. This would not be possible in a classical oven.

The plasma center in warm plasmas is characterized by a much higher temperature (at least up to 6000 K), needed to ensure adequate conductivity. This is much above the most suitable temperature for efficient chemical conversion (typically around 3000 K), and thus, the chemically active region for the various gas-phase chemistries discussed in this thesis is located in the periphery, around the hot plasma core. Therefore, tuning the temperature gradient within the plasma edge by means of the outer layers of the gas flow is crucial. This has been explored in experiments before, perhaps accidentally [137]. In this paper, my first co-authored paper, we confined the APGD using a ceramic piece, which greatly increased the conversion and reduced the energy cost. Because modeling

the plasma as a 1D plug flow was the only option at that time, the increased performance was attributed to more gas passing through the plasma [135]. Retrospectively, this confinement also increases the cold-gas flow rate adjacent to the plasma, raising the temperature and thus the species gradients, thereby allowing more diffusive transport between the plasma and the cold outer flow and increasing the conversion. Still, the confinement was such an improvement that we kept it for the DRM experiments with O₂ addition, presented in Chapter 3.

In my opinion, multidimensional fully coupled CFD models are the preferred way to describe warm plasmas, and to calculate performance metrics, such as conversion, EC and product selectivity, rather than using global models. While it is still not possible to model complex transient plasmas, like CH₄ pulses, in 2D, a better understanding of continuous arc plasma, glow discharge, or microwave plasma benefits much more from a multidimensional model than from a global plasma kinetics model. On the other hand, we believe that global plasma models can still have their value. Exploring an extensive parameter space, as in Chapter 4, remains a good use of global models. However, such models should not be applied to a specific atmospheric-pressure contracted plasma experimental setup, because the global (uniform) character of such models can obviously not capture the non-uniform plasma properties.

The future aim of plasma modeling should be to model plasma systems before experiments are carried out. For instance, we can start aiming to change product selectivity by modeling systems with carefully controlled temperature gradients, using flow dynamics or temperature-controlled insulation. Indeed, computational scanning of parameters is much easier and faster than trial-and-error experiments, saving an immense cost. However, this is only possible with truly predictive models, which must first be extensively validated with experiments, within a broad range of conditions.

Overall, the classical trial-and-error approach only works for simple systems, and if it is simple, it has probably already been done. Understanding what happens and why, is the only way forward when we aim to really make progress with increasingly complex systems.

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Conference contributions

Wilhelm und Else Heraeus Seminar, April 23 – 27, 2023, Bad Honnef, Germany. Poster presentation: “Effect of O₂ on the dry reforming of methane in an atmospheric pressure glow discharge”

Antwerp-Maastricht Plasma Symposium (AMPS), February 2, 2024, Maastricht, Netherlands. Oral presentation: “Addition of Oxygen in Dry Reforming of Methane”

26th International Symposium of Plasma Chemistry (ISPC), June 15 – 20, 2025, Minneapolis, USA. Oral presentation: “Effect of turbulence on NH₃ cracking: a Gliding Arc Plasmatron study”.

Winnaars zijn verliezers die niet opgeven.

P. Maerivoet