

CFD Simulation of Methane Pyrolysis in Plasma Reactor for CO₂-free Hydrogen

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Zusammenfassung

Die Reduzierung von Treibhausgasemissionen und die Verlangsamung der globalen Erwärmung gehören zu den wichtigsten Herausforderungen unserer Zeit, insbesondere in den Bereichen Industrie, Verkehr und Landwirtschaft. Eine vielversprechende Lösung ist die Umstellung auf Wasserstoff als sauberen Energieträger.

Unter den verschiedenen Methoden zur Wasserstofferzeugung bietet türkisfarbener Wasserstoff, der durch Methanpyrolyse erzeugt wird, einen vielversprechenden Weg zur Reduzierung der CO₂-Emissionen. Wenn dieser Prozess in Plasmareaktoren durchgeführt wird, die mit erneuerbaren Energien betrieben werden, ermöglicht er die Produktion von CO₂-freiem Wasserstoff.

Diese Arbeit präsentiert CFD-Simulationen der Methanpyrolyse in zwei Arten von Plasmareaktoren: Gliding-Arc-Plasma (GAP) und Mikrowellenplasma (MW). Die 0D-Sensitivitätsanalysen ergaben, dass aufgrund der hohen Plasmatemperaturen (3000 – 4000 K) thermische Reaktionen gegenüber Elektronenstoßreaktionen dominieren. In detaillierteren 2D- und 3D-Simulationen wurde das Plasma daher als Wärmequelle modelliert, um die Reaktionsdynamik zu untersuchen und das Reaktordesign sowie die Betriebsbedingungen zu optimieren. In diesen Modellen wurde das MW-Plasma durch einen Gaußschen Peak dargestellt, während das GAP-Plasma als „künstlicher Lichtbogen“ modelliert wurde. Durch diesen Ansatz konnte die Methanumwandlung im GAP-Reaktor von 35 auf 44 % verbessert werden. Die Simulation identifizierte auch Zonen mit erhöhter Nebenproduktbildung innerhalb des MW-Plasmareaktors. Diese Erkenntnisse können zu zukünftigen Verbesserungen im Reaktordesign beitragen und so die Gesamteffizienz steigern.

Zusätzlich wurden Simulationen für Surface Dielectric Barrier Discharge (SDBD) unter Verwendung eines Gasgemisches aus Sauerstoff, Stickstoff und Wasserstoff durchgeführt. Im Vergleich zur Methanpyrolyse waren bei diesem Gemisch weniger chemische Reaktionen vorhanden, sodass keine Vereinfachung der Plasmamodellierung erforderlich war. Der Schwerpunkt der Simulation lag auf den Plasmaentladungseffekten, insbesondere dem Einfluss des Ionenwinds auf die Gasumwandlung. Da die Gastemperatur im SDBD-Reaktor deutlich niedriger war als in den GAP- und MW-Reaktoren, zeigten die Simulationen deutlich den Unterschied zwischen kaltem und warmem Plasma.

Abstract

Reducing greenhouse gas emissions and slowing global warming are among today's most pressing challenges, particularly in the industrial, transportation, and agricultural sectors. One promising solution is the transition to hydrogen as a clean energy carrier.

Among the various methods of hydrogen production, turquoise hydrogen, generated through methane pyrolysis, offers a promising pathway to reduce carbon emissions. When this process is carried out in plasma reactors powered by renewable energy, it enables the production of CO₂-free hydrogen.

This work presents CFD simulations of methane pyrolysis in two types of plasma reactors: gliding arc plasma (GAP) and microwave plasma (MW). The 0D sensitivity analyses revealed that thermal reactions dominate over electron impact reactions due to high plasma temperatures (3000 – 4000 K). Consequently, in more detailed 2D and 3D simulations, plasma was modeled as a heat source to explore the reaction dynamics and optimize reactor design and operating conditions. In these models, the MW plasma was represented by a Gaussian heat peak, while the GAP plasma was modeled as an "artificial arc". This approach improved methane conversion in the GAP reactor from 35 to 44 %. The simulation also identified the zones of increased by-product formation within the MW plasma reactor. These findings can inform future improvements in reactor design, helping to enhance overall efficiency.

Additionally, simulations were conducted for surface dielectric barrier discharge (SDBD) plasma using a gas mixture of oxygen, nitrogen, and hydrogen. Compared to methane pyrolysis, this mixture involved fewer chemical reactions, so no simplification of the plasma modeling was necessary. The focus of the simulation was on the plasma discharge effects, specifically the influence of ionic wind on gas conversion. Since the gas temperature in the SDBD reactor was significantly lower than in the GAP and MW reactors, the simulations clearly demonstrated the difference between cold and warm plasmas.

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List of Abbreviations

APPJ	Atmospheric plasma pressure plasma jet
CCUS	Carbon Capture, Utilization and Storage
CFD	Computational fluid dynamics
DBD	Dielectric barrier discharge
DNS	Direct numerical simulation
DSMC	Direct simulation Monte Carlo
EEDF	Electron energy distribution function
EAA	European Environment Agency
EU	European Union
GAP	Gliding Arc Plasma
GHG	Greenhouse gas
HPEM	Hybrid plasma equipment model
LTE	Local thermal equilibrium
MW	Microwave plasma
NTP	Non-thermal plasma
PIC	Particle-In-Cell
RANS	Reynolds-Averaged Navier-Stokes
RSM	Reynolds Stress Model
SDBD	Surface dielectric barrier discharge
SMR	Steam methane reforming
SST	Shear Stress Transport
0D	Zero-dimensional model
1D	One-dimensional model
2D	Two-dimensional model
3D	Three-dimensional model

List of Symbols

Symbol	Unit	Definition
a_1 - a_5	[-]	NASA polynomials
$a_{ij}^{(1)}, a_{ij}^{(2)}$	[-]	Stoichiometric coefficient
A_j	[cm ³ /mol/ s]	Frequency factor for j reaction
B_K	[-]	Karman constant
c	[m/s]	Speed of sound
C_p	[J/mol/K]	Specific heat capacity at constant pressure
c_p	[J/kg/K]	Mass specific heat capacity at constant pressure
C_v	[J/mol/K]	Specific heat capacity at constant volume
c_v	[J/kg/K]	Mass specific heat capacity at constant volume
$C(f(\varepsilon))$	[-]	Collisional term
$CD_{k\omega}$	[-]	Cross-diffusion term
d	[m]	Characteristic length
$D_{i,Ar}$	[m ² /s]	Diffusion coefficient of i species and Argon
D_k	[m ² /s]	Drift diffusion coefficient of species k
$\vec{e}$	[C]	Electron charge
E	[J]	Internal energy
e	[J/kg]	Specific internal energy
E	[V/m]	Electric field
E_{avg}	[eV]	Average energy of electrons
$E_{a,j}$	[kJ mol ⁻¹]	Activation energy
$f(\varepsilon)$	[eV ^{-3/2}]	Electron energy distribution function
F	[-]	Degrees of freedom
f	[N]	Body forces
F_{EH}	[N/m ³]	Electro hydrodynamic body force
F_{pulse}	[N/m ³]	Pulse-averaged electro hydrodynamic body force
F_1	[-]	Blending function
F_2	[-]	Blending function
H	[J]	Enthalpy energy
h	[J/kg]	Specific enthalpy
$I(\varepsilon)$	[-]	Spitzer integral
$J(\varepsilon)$	[-]	Spitzer integral

k	[J]	Kinetic energy
k	[-]	Heat capacity ratio
k_B	[J/K]	Boltzmann constant
K_H	[W/m/K]	Heat conduction coefficient
k_i	[W/m/K]	Thermal conductivity of species i
k_j	[mol/m/ s]	Reaction rate constant for j reaction
k_K	[-]	Karman constant
M_i	[g/mol]	Molecular weight
m_e	[kg]	Mass of electron
m_p	[kg]	Mass of particle
Ma	[-]	Mach number
n	[mol]	Number of moles
n_e	[m ⁻³]	Number of electrons
n_I	[m ⁻³]	Number of ionic species
n_k	[1/m ³]	Number density of species k
n_N	[m ⁻³]	Number of neutral species
n_0	[mol/mol]	Initial mole fraction
n_0	[m ⁻³]	Ground-state density of the neutral molecule
p	[Pa]	Pressure
$\bar{p}$	[Pa]	Time-averaged mean pressure
p'	[Pa]	Fluctuating pressure component
$P_{\text{consumption}}$	[W]	Consumed power by plasma
p_{crit}	[Pa]	Critical pressure
P_{Joules}	[W]	Joules heating
P_k	[J/kg]	Turbulence kinetic energy
Pr	[-]	Prandtl number
q_{eff}	[J/kg/s]	Turbulent heat flow
Q_{ext}	[W]	External energy source
Q_{Joules}	[W]	Joules heating
Q_{supply}	[W]	Power applied
q_{plasma}	[W/m ³]	Heat source from MW plasma
r	[m]	Radius of the outlet tube
R	[J/mol/ K]	Gas constant
R_{spec}	[J/kg/ K]	Specific gas constant

Re	[-]	Reynolds number
S_{H_2/C_2H_2}	[%]	Selectivity of H_2 , C_2H_2 or other products
t	[s]	Time
T	[K]	Temperature
T_{boil}	[K]	Boiling point
T_{crit}	[K]	Critical temperature
T_e	[K]	Mean electron temperature
T_g	[K]	Gas / heavy particle temperature
T_i	[K]	Ion temperature
T_k	[K]	Temperature of species k
T_p	[s]	Pulse interval for DBD plasma
u_p	[m/s]	Particle velocity
u	[m/s]	Velocity vector in Cartesian coordinates (x, y, z)
$\bar{u}$	[m/s]	Time-averaged mean velocity
u'	[m/s]	Fluctuating velocity component
u_τ	[m/s]	Friction velocity
V	[m ³]	Volume
x_i	[mol/mol]	Molar fraction of species i
X_{CH_4}	[%]	Conversion of CH_4
$y_\perp$	[-]	Distance normal to the wall
y^+	[-]	Dimensionless wall distance
u^+	[-]	Dimensionless velocity
u_τ	[m/s]	Friction velocity
z_L	[m]	Plasma torch length

List of Greek Symbols

Symbol	Unit	Definition
α_{eff}	[m ² /s]	Effective thermal diffusivity
σ_j	[cm ²]	Collision cross section data for j reaction
σ_i	[m]	Characteristic potential length
σ_{ij}	[cm ²]	Collision cross section data for i → j transition
σ_m	[cm ²]	Momentum transfer cross section of electron-neutral
σ	[-]	Gaussian standard deviation
Γ	[-]	Incomplete Gamma function
Γ_k	[1/m ² /s]	Flux of species k
δ_{ij}	[-]	Kronecker delta
σ_i	[Å]	Characteristic potential length
ε	[eV]	Electron energy
ε_k	[eV]	Mean electron energy
ε_i	[J]	Minimum potential energy
$\varepsilon_{\text{medium}}$	[-]	Medium permittivity
λ_d	[m]	Debye length
μ_D	[J]	Dipole moment
μ_k	[m ² /V/s]	Mobility coefficient of species k
μ_i	[Pa s]	Dynamic viscosity
μ_t	[Pa s]	Turbulent viscosity
ρ_f	[C/m ³]	Charge density
ρ_{crit}	[mol/l]	Critical density
ρ	[kg/m ³]	Density
τ_w	[Pa]	Wall shear stress
τ_{ij}^{Re}	[Pa]	Reynolds stress tensor
ν_t	[m ² /s]	Kinematic viscosity
ν_k	[1/s]	Elastic collision frequency
ν_e	[1/s]	Momentum transfer frequency
$\Omega^{(1,1)*}$	[-]	Collision integral
$\Omega^{(2,2)*}$	[-]	Collision integral
τ^{Re}	[-]	Reynolds stress tensor
ω	[1/s]	Dissipation rate

θ_k	[eV]	Energy loss from elastic collisions
φ	[V]	Electric potential
σ_{DF}	[-]	Distribution factor

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Chapter 2	2.2	modified in parts from	[a]
	2.3	modified and expanded in parts from	[b]
		modified and expanded in parts from	[B, c]
		modified and expanded in parts from	[d]
	2.5.5	modified and expanded in parts from	[a, e]
Chapter 3	3.2	modified and expanded in parts from	[f]
	3.3	modified in parts from	[A]
	3.3	data collection from	[g]
	3.3	modified and expanded in parts from	[b, f]
	3.4	modified in parts from	[A]
	3.5	modified and expanded in parts from	[B, e]
	3.6	modified and expanded in parts from	[A, e, h]
Chapter 4	4.2	modified and expanded in parts from	[c]
		data collection from	[g]
	4.3	modified and expanded in parts from	[c]
	4.4	modified and expanded in parts from	[c]
	4.5	modified and expanded in parts from	[B, c]
Chapter 5	5.3	modified and expanded in parts from	[d]
	5.4	modified and expanded in parts from	[C, d]
	5.4	modified and expanded in parts from	[d]

Publications

- [A] Magazova, A.; Böddeker, S.; Bibinov, N.; Agar, D. W. Systematic Simulation Strategy of Plasma Methane Pyrolysis for CO₂-free H₂. *Chem. Ing. Tech.* **2022**, 94 (5), 690–700. DOI: <https://doi.org/10.1002/cite.202100181>
- [B] Magazova, A.; Agar, D. W. Improvement of Plasma Reactor Design for Methane Pyrolysis by Simulation. *Chem. Ing. Tech.* **2023**, 95 (5), 780–784. DOI: <https://doi.org/10.1002/cite.202200188>
- [C] Ollegott, K.; Wirth, P.; Oberste-Beulmann, C.; Sakthi, G. S. M.; Magazova, A.; Hermanns, P.; Peters, N.; Schücke, L.; Bracht, V.; Agar, D. W.; Awakowicz, P.; Muhler, M. Investigation of Flow Characteristics in a Twin-Surface Dielectric Barrier Discharge Reactor by Schlieren Imaging. *J. Phys. D Appl. Phys.* **2023**, 56, 265201. DOI: <https://doi.org/10.1088/1361-6463/acc956>

Data collection and simulation as part of student theses

- [a] Thierfelder, A. Simulation of reverse vortex flow and gliding arc plasma in OpenFOAM, Master thesis, Dortmund, 2020.
- [b] Li, S. A systematic simulation approach of the gliding arc plasma reactor with the reverse vortex flow, Master thesis, Dortmund, 2020.
- [c] Plischka, W. Simulation of a microwave plasma reactor with a methane/argon mixture, Master thesis, Dortmund, 2022.
- [d] Mani Sakthi, G. S. Reaction zone investigation of surface dielectric barrier discharge (SDBD) reactor through CFD simulations with the experimental validation, Master thesis, Dortmund, 2020.
- [e] Luttmann, T. Gliding arc plasma reactor simulation in OpenFOAM for methane pyrolysis, Master thesis, Dortmund, 2022.
- [f] Afsahnoudeh, R. Simulation of gliding arc plasma reactor for pyrolysis of methane with argon as carrier gas, Master thesis, Dortmund, 2021.
- [g] Schulze, J. P. Optimization and carbon characterization of CO₂-free methane pyrolysis using microwave plasma and gliding arc plasmatron, Protocol for the practical course, Dortmund, 2021.
- [h] Wiltfang, T. Study of the reverse vortex fluid flow dependence on the reactor geometry, Bachelor thesis, Dortmund, 2020.

1. Motivation

Global warming is a major problem with severe consequences for the environment and society. This fact is aggravated by the heavy industrial development, growing energy consumption, and the rapid increase in carbon dioxide emissions, leading to a number of ecological and economic issues [1]. One of the most significant contributors to global warming is the release of carbon dioxide from fossil fuel combustion. In fact, the anthropogenic contribution to global warming between 2000 and 2019 is approximately 1.18 °C above preindustrial levels, this trend is accelerating at a rate of 0.28 °C per decade due to human activities associated with energy production and consumption [2]. Moreover, the existing energy systems in many parts of the world are largely based on the combustion of fossil fuels, which release significant amounts of carbon dioxide and other greenhouse gases (GHG) into the atmosphere [3]. This impact could be seen in environmental disasters such as intense heat, droughts, hurricanes, fires, floods, and rising sea levels, which occur more frequently in the last decades [4] [5]. The influence on global warming is also evident in the context of energy consumption and energy efficiency. According to the European Environment Agency (EEA), in 2022, the final energy consumption in the European Union (EU) was 3.93×10^{10} GJ, which is 2.8 % lower compared to 2021. However, it is still 23.3 % away from the 2030 target [6]. In the last decade, the primary energy production in the EU coming from solid fossils, oil and gas, and nuclear energy has been decreasing. The energy production from natural gas declined steeply by 63.1 % over the last decade, and a comparable decrease is seen for energy from solid fossil fuels and petroleum, which are down by 39.1 % and 36.0 %, respectively. The energy generation from renewable sources, on the other hand, has significantly risen by 48.2 % over the last 10 years, and waste-to-energy plants production grown by 24.5 % in the same period. Despite the dropping tendencies, oil and gas are still major energy sources in Europe [7]. In 2022, CO₂ emissions from fossil fuel combustion in the EU resulted in 2.4 Gigatons, which is 2.8 % lower than in 2021 [8]. This progression should be maintained in order to reach 55 % GHG reduction target in 2030 [9].

To address the challenges posed by global warming and GHG emissions, several worldwide agreements have been established to mitigate its impact and limit temperature increases. The Paris Agreement, a landmark international treaty adopted in 2015 at the 21st Conference of the Parties under the United Nations Framework Convention on Climate Change, represents a significant global effort to combat climate change. The agreement aims to limit global warming to well below 2 °C above pre-industrial levels and pursue efforts to limit the temperature increase to 1.5 °C. This ambitious target reflects the urgent need to address the adverse effects of global warming and mitigate its impact on the planet [10] [11]. The

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agreement has stimulated research aimed at solving the issue and investigating strategies to address the challenges associated with global warming [12]. In addition to the international agreements, carbon sequestration has been proposed as a means of reducing atmospheric carbon to mitigate global warming and climate change. However, these strategies underscore the importance of implementing measures to actively remove CO₂ from the atmosphere, contributing to the overall efforts to combat global warming [13]. The urgency to tackle the effects of global warming has led to increasingly demanding regulations and a worldwide compromise to address the issue. This reflects a growing recognition of the need for coordinated and decisive action to mitigate the impacts of global warming and limit temperature increases, emphasizing the global nature of the challenge and the necessity for collective efforts to address it [14].

The reduction of CO₂ emissions is one of the global challenges of the XXI century. In parallel to CO₂ capture and sequestration, the production of CO₂ free energy is a key solution for this environmental problem. Hydrogen is increasingly recognized as a key energy carrier in the transition toward a sustainable and low-carbon energy system. As countries strive to decarbonize various sectors, including transportation, industrial processes, and power generation, the role of hydrogen as an energy carrier is expected to grow significantly [15]. Hydrogen is a clean energy carrier that possesses the potential of becoming a key factor in lowering carbon emissions. Hydrogen can be generated by a variety of methods, which include steam methane reforming (SMR), electrolysis, biomass or fossil-fuel gasification, and methane pyrolysis [16]. Therefore, it is classified into grey, blue, turquoise, pink, and green hydrogen, which depends on the methodology and carbon emissions level as shown in Figure 1-1.

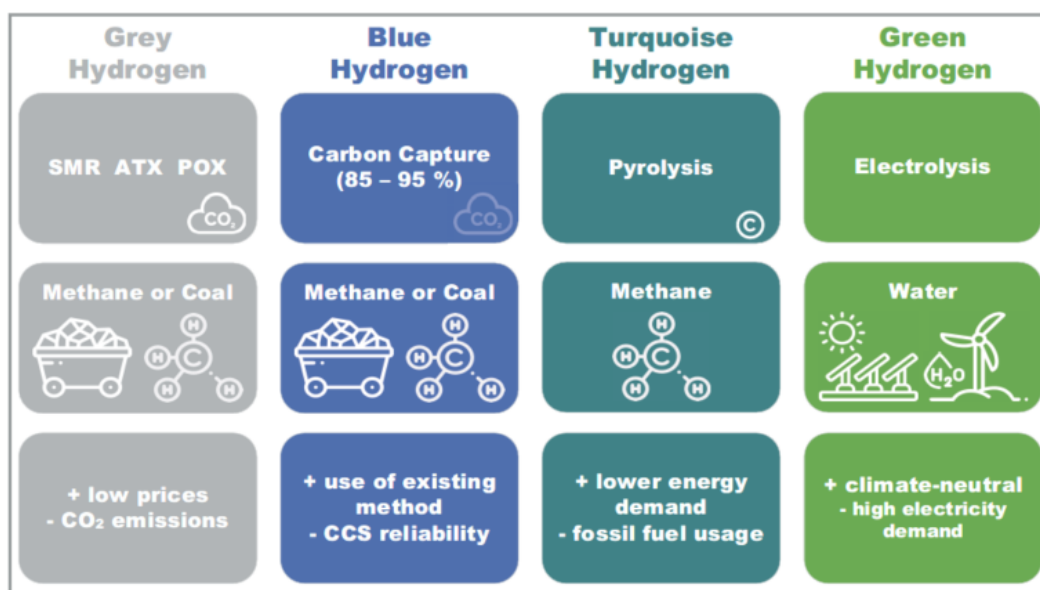
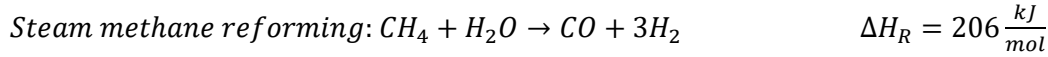
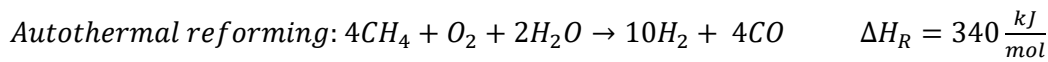
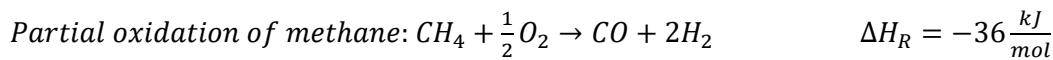
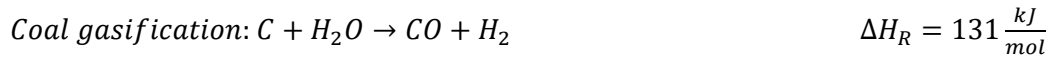
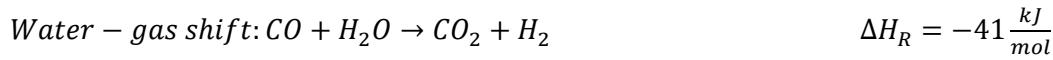


Figure 1-1 Hydrogen production classification [17].

Grey hydrogen, which accounts for a major part of hydrogen produced, is a product of SMR or fossil fuels gasification and accompanied by large CO₂ footprint. The following reactions are a few examples of grey hydrogen production [18] [19]:



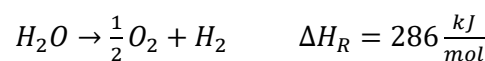
following with subsequent:



All of the reactions above produce CO₂ or CO as by-products. CO subsequently reacts with water and oxygen and contributes to CO₂ generation. Thus, the hydrogen produced is classified as grey hydrogen.

Grey hydrogen is turned into blue hydrogen, when the carbon capture and storage is utilized to eliminate CO₂. Since it does not solve the emissions problem directly, and only prevents the release into the environment, blue hydrogen raises many controversies. Today carbon capture and storage (CCUS) units mitigate around 45×10^6 tons of CO₂, which is only 0.1 % of all GHG emissions. Even in the IEA Roadmap to Net Zero Emissions by 2050, the CCUS contribution is only estimated at 8 % of total CO₂ emissions [20]. Which means that this pathway is probably not feasible.

Green hydrogen is the one produced using renewable energy sources such as solar, wind, geothermal and hydro power, where hydrogen is created by splitting water into hydrogen and oxygen with no CO₂ emissions.



Pink hydrogen is similar to green hydrogen, with the difference that electrolysis is powered by nuclear energy.

Turquoise hydrogen is a relatively new classification, where hydrogen is produced by methane pyrolysis. Here, the hydrogen source is fossil fuel, however the carbon emissions are limited, since the generated carbon is in solid state [21] [22]. In comparison to water electrolysis, the

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energy demand of methane pyrolysis is significantly lower, and this is one of the advantages of methane pyrolysis in plasma.



Methane pyrolysis is a promising technology for CO₂-free hydrogen production, serving as a bridge from fossil fuels to renewable energies [23] [24]. Unlike the other technologies using fossil resources, such as coal gasification or steam methane reforming, methane pyrolysis offers the significant advantage – it produces CO₂-free hydrogen [23], because carbon is in the solid state. However, there are challenges associated with methane pyrolysis, such as the need for high temperatures (1000 - 1100 °C), which can cause technological problems in designing pyrolysis facilities [25]. One of the methods to obtain high energy is methane pyrolysis in plasma. Plasma is a fourth state of matter, which contains large concentration of reactive radicals, ions and electrons, and can achieve 10⁴ K magnitude temperature. Plasma can be generated by electricity, which is produced by alternative sources of energy. This makes plasma pyrolysis a more attractive solution. Compared with conventional steam methane reforming, this technology offers a promising pathway for decarbonizing industrial hydrogen production from natural gas through the elimination of direct CO₂ emissions [26]. Additionally, the potential for solid carbon, ethene, and ethyne production alongside hydrogen highlights the versatility of methane pyrolysis [27]. In conclusion, methane pyrolysis presents a promising pathway for CO₂-free hydrogen production, offering a bridge from fossil fuels to renewable energies. Figure 1-2 shows an example of the incorporation of the plasma reactor for CO₂ free hydrogen production [28].

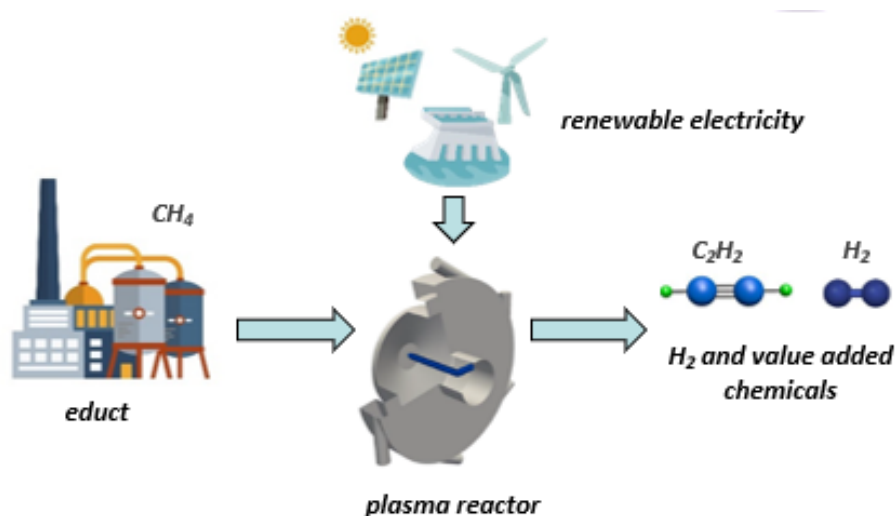


Figure 1-2 Plasma reactor integration for sustainable H₂ [28].

Plasma reactors for sustainable hydrogen production from methane have several advantages and disadvantages. The use of these advanced reactors leverages the unique characteristics of plasmas to facilitate chemical reactions, prominently highlighting the potential contribution of plasma-assisted processes to a green hydrogen economy.

One of the primary advantages of plasma reactors is their capability for high conversion efficiency of methane into hydrogen. For instance, studies have demonstrated that non-equilibrium plasma techniques can achieve significant methane conversions and subsequently high hydrogen production rates [29]. In these reactors, methane can be dissociated effectively due to the energetically charged electrons generated within the plasma, leading to the formation of reactive intermediate species that enhance reaction pathways for hydrogen generation [30]. Furthermore, the plasma reactors are inherently flexible and can rapidly adapt to the fluctuations in the renewable energy supplies, which is essential for integrating the green hydrogen production into evolving energy grids powered by recurrent renewable resources [29] [31].

Additionally, the environmental benefits of hydrogen produced via plasma techniques are notable. Specifically, when powered by renewable energy sources, methane pyrolysis in atmospheric pressure plasma reactors can yield hydrogen and solid carbon as byproducts while avoiding CO₂ emissions, thus addressing a critical need for low-emission energy solutions. Moreover, plasma reactors can enable methane reforming processes without the extensive need for external heat inputs, instead utilizing the exothermic nature of plasma-generated reactions to drive conversions. No heating surface is necessary to convert methane, since the reactive species in plasma are the drivers for the reactions [32] [29] [24].

However, the advantages come with the significant drawbacks. One primary concern is the high energy consumption associated with operating plasma reactors. The operational costs for electricity can be considerable, and studies have identified that these costs can render plasma processes less economically competitive relative to traditional catalysis methods without the complementary advancements in the reactor efficiency and energy sourcing [33]. Nevertheless, over the last years an increase in electricity surplus can be noticed, which results in the negative electricity prices in Germany. Figure 1-3 shows that in 2024 approximately 457 hours were reported with negative prices, which is around 5 % of 2024. This is due to the rapid growth of the sustainable energy sources. In 2024, 62.7 % of electricity was produced from renewable energy sources, mainly from the wind turbines and solar panels [34]. The limitations in storage capacity during windy or sunny weather lead to a higher electricity supply than demand. Therefore, the electricity costs sink to the negative margin as given in Figure 1-3. The plasma reactors can convert methane immediately upon the power

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supply and can be turned off rapidly without damaging the equipment. Hence, one of the ways to store the surplus from renewable electricity is via hydrogen produced by methane pyrolysis in plasma reactors.

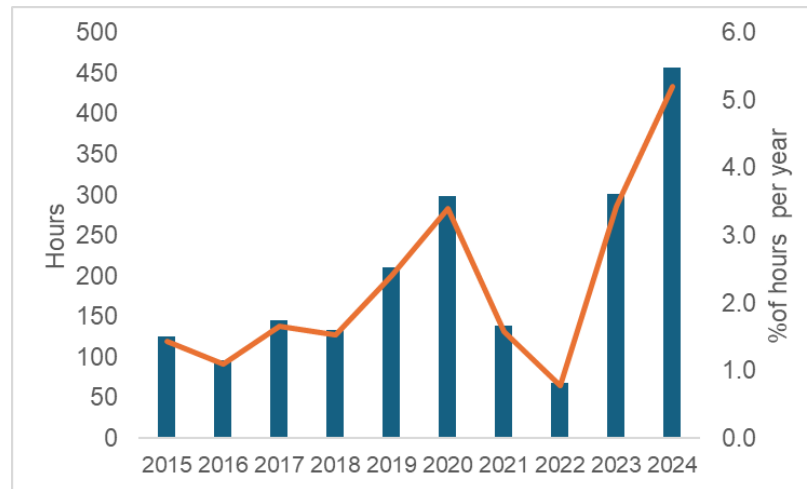


Figure 1-3 Annual hours with negative wholesale electricity prices in Germany [35].

Additionally, while the plasma reactors can effectively improve conversion rates, they also exhibit challenges in stability and control. The applied operating conditions can lead to variability in the output products, making consistent product quality a concern [36]. Furthermore, the durability of the reactor components is often compromised due to the aggressive nature of plasma environments, potentially leading to the increased maintenance and replacement costs over time [37]. The phenomenon of erosion in the plasma reactors, particularly those operated under the fusion conditions or in industrial applications, is a critical subject of study due to its implications for reactor performance and durability. Erosion occurs primarily due to the plasma-wall interactions, where the energetic ions and atoms emitted from the plasma bombard the reactor walls, leading to physical and chemical material degradation [38]. Therefore, it is vital to understand the plasma technology, to tackle the arising challenges. The simulations help to understand the working principle of the plasma reactors for methane pyrolysis. Additionally, the weaknesses of the reactor can be visualized by the simulations. Therefore, the results obtained from the simulations help to optimize the reactor design and operating conditions, which might help the methane pyrolysis in plasma to become a viable alternative to green hydrogen. The experiments reported the energy input required for hydrogen production of 327 kJ/mol_{H₂} and 623 kJ/mol_{H₂} for the gliding arc plasma and microwave plasma respectively, which is still significantly higher than by the industrial steam-methane reforming, which is 69 kJ/mol_{H₂} [39]. On the other hand, for steam-methane reforming, for each kilogram of H₂ produced, there are 8.47 kg of CO₂ emissions generated [40]. The latest CO₂ prices in Germany have been increased from 45 €/t CO₂ to

55 €/t CO₂, between 2024 and 2025, and will be increasing as a climate change countermeasure agreed by the EU [41]. Therefore, the economic advantage of industrially widespread grey hydrogen production is diminishing.

On the contrary, the latest expansion of the renewable energy sector in Germany is advantageous for the methane pyrolysis as a CO₂-free hydrogen alternative. The comparison between the CO₂ footprint and H₂ production costs for the different hydrogen production technologies is shown in Figure 1-4.

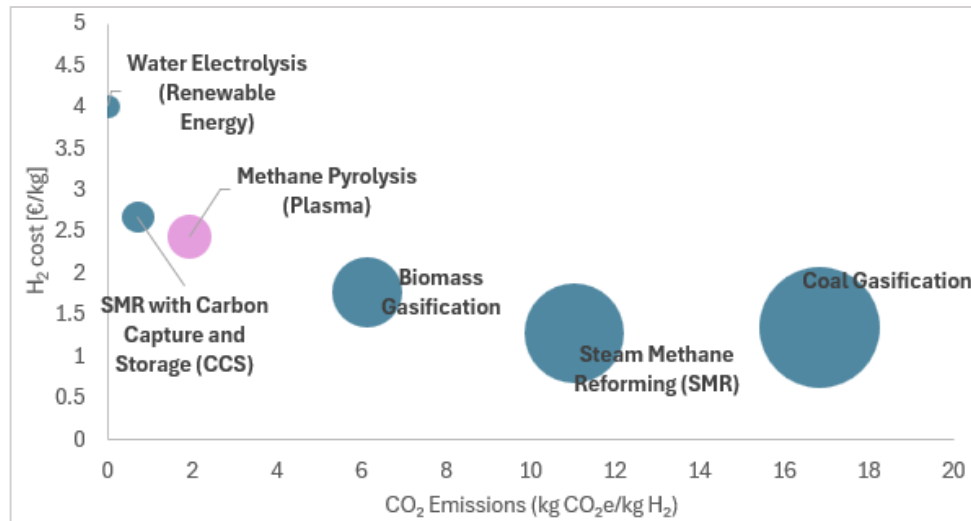


Figure 1-4 H₂ production cost and CO₂ emission for different hydrogen production methods [42] [43].

When compared to the conventional hydrogen production technologies, methane pyrolysis in plasma is still more expensive than the steam methane reforming or coal gasification. This is due to the utilization of electricity for the plasma generation. On the other hand, when the electricity surplus exists, the electricity price is negative, thus, methane pyrolysis becomes more attractive. Moreover, the development of more sustainable and environmentally friendly solutions is essential for achieving further reductions in CO₂ emissions. Thus, methane pyrolysis in plasma can be a feasible solution for the CO₂ level reduction.

The thermal plasma technology has already demonstrated its viability for the large-scale methane pyrolysis in the industrial settings. Two notable examples of such implementations are the Kvaerner process and the Hüls process, both of which were developed and operated at large scales. The Kvaerner process utilized a direct current plasma arc to decompose methane into hydrogen and solid carbon. This method generated an annual hydrogen production capacity of approximately 70 million Nm³ [44]. In contrast, the Hüls process employed an alternating current plasma arc, not for methane but for coal pyrolysis. This process converted coal into the valuable chemical products such as ethyne and ethene [45].

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A recent example of the industrially scaled methane pyrolysis is the technology developed by Monolith Materials in the US [44]. Monolith Materials uses alternating current plasma arcs to thermally decompose methane into turquoise hydrogen and solid carbon, without emitting CO_2 . The company claims that this process is powered by 100% renewable electricity, making it both environmentally and economically sustainable. The company operated at 5 kt of hydrogen per annum in 2021 and planned to extend the production mainly focusing on the carbon black production increase [46].

The aim of this work is to provide a comprehensive portrayal of plasma reactors through the application of the Computational Fluid Dynamics (CFD) simulations. This involves the critical task of selecting a representative chemical reaction set, a process that is inherently challenging due to the highly reactive nature of plasma. Moreover, plasma reactors exhibit substantial gradients in temperature, concentration, and velocity, which necessitate a meticulous attention to the definition of the computational domain. Therefore, careful attention has been paid to the mesh quality and its resolution, since it can significantly influence the simulation accuracy. The governing equations necessary for simulating the plasma reactors have been identified, including heat and mass transfer equations, as well as the plasma-specific equations. Finally, by analyzing the results derived from these CFD simulations and validating and comparing them with the experimental data, it was possible to identify a range of potential improvements. These improvements include modifications to the reactor geometry and fine-tuning of the operating conditions, which are all intended at enhancing the conversion of methane. The experiments confirmed a higher methane conversion and plasma stability due to these alterations, that were identified with the aid of the simulations. The simulation results are discussed in this work.

2. Theoretical background

2.1 Introduction

Plasma is a state of matter that forms when a gas is energized to the point where its atoms lose electrons. This process creates a mixture of free electrons, ions, and neutral species. Unlike the three classical states of matter - solid, liquid, and gas - plasma is electrically charged and interacts strongly with the electromagnetic fields [47].

This chapter explains the theory behind plasma chemistry and different classifications of plasma. The theoretical background behind fluid flow modeling and plasma simulation approaches is explained. Modeling of plasma is a complex task due to the intricate interplay of physical, chemical, and electromagnetic phenomena. Plasma exhibits a wide range of physical properties, including non-equilibrium conditions, high energy densities, and rapid temporal and spatial variations. These properties make it difficult to develop accurate mathematical models that capture the full behavior of plasma. Moreover, plasma involves complex chemical reactions, including electron impact reactions and radical recombination reactions. The electron impact reactions produce the radicals, and then these radicals recombine to products, such as hydrogen, ethane, ethene and ethyne. The electron impact reactions are activated by the electrical discharge, whereas the radical recombination reactions are temperature dependent [48]. Therefore, simulating plasma requires solving the coupled equations for fluid dynamics, electromagnetic fields, and the species balances affected by the chemical reactions. These simulations are computationally expensive and time-consuming. Therefore, in this chapter the applied modeling methodologies are explained in order to simulate the gliding arc plasma reactor, microwave plasma reactor and the surface dielectric barrier discharge plasma reactor.

2.2 Plasma classification

Plasma is created by supplying enough energy to the neutral gas so that electrons detach from the species and positive ions are formed. The process is called ionization, resulting in the electrically conductive plasma, which can be manipulated by the electric and magnetic fields [49].

Plasma is classified into the high temperature plasma (lightning, aurora, sun) and low temperature plasma (fluorescent lamps and neon signs). The low temperature plasma is divided into the thermal plasma and non-thermal plasma, which is defined by the thermodynamic equilibrium state of particles [50]. In this work the low temperature plasma is applied for methane pyrolysis, therefore, it will be discussed in more detail.

2. Theoretical background

The thermal plasmas are in so-called local thermal equilibrium (LTE). LTE is when the mean electron temperature T_e and the temperature of relatively heavier particles T_G are equal, and their magnitude is ca. 10^4 K, or equivalent 1 – 20 eV [51].

The electron temperature T_e is calculated as follows [49]:

$$T_e = \frac{E_{avg} \times 1.6 \times 10^{-19} \left[\frac{J}{eV} \right]}{1.38 \times 10^{-23} \left[\frac{J}{K} \right]} \cong E_{avg} [eV] \times 11600 K \quad (2-1)$$

Equation (2-2) is derived from the electrons' kinetic energy with Maxwellian velocity distributions:

$$E_{avg} = \frac{1}{2} m_p u_p^2 = \frac{3}{2} \times k_B \times T_e \quad (2-2)$$

where m_p – mass of particle, u_p – particle velocity, $k_B = 1.38 \times 10^{-23} \left[\frac{J}{K} \right]$ Boltzmann constant.

Another parameter which is used for the plasma classification is a degree of ionization (2-3):

$$\frac{n_I}{n_I + n_N} \quad (2-3)$$

where the number of charged n_I and neutral species n_N is considered. The degree of ionization is proportional to the number of electrons n_e , which affects the behavior of plasma as well. These free electrons transfer energy by collision, and initiate further ionization, excitation, dissociation and chemical reactions [51]. For simplification, it is often assumed that $n_I \ll n_N$, yielding a straightforward ratio of ions to neutral species. This ratio is the degree of ionization and plasmas are categorized as highly ionized when the ratio is higher than 10^{-3} , or weakly ionized when it is less than 10^{-3} [49]. The degree of ionization is dependent on the dominant collision reactions. Specifically, a distinction is made between electron-ion collisions and electron-neutral species collisions. Plasma is considered fully ionized when electron-ion collisions occur more frequently than electron-neutral collisions. Conversely, if electron-neutral collisions dominate, the plasma is classified as partially or weakly ionized [51].

The reactions occurring in the thermal plasma are thermally driven. The typical examples of the thermal plasma are the direct current plasma arcs, plasma torches, RF inductively coupled discharge etc. The thermal plasma is widely used in plasma smelting, coating, and welding, where high temperature is required. It can generate high electron density, but the equipment is very costly and requires high power [25].

On the other hand, there are non-thermal or cold plasmas (NTP) that are in non-LTE state. The temperature of the ions and neutrals can be as low as room temperature, whereas the electron temperature is much higher. This occurs when n_e is low, and so is the energy transferred by collisions. Hence, due to insufficient energy for equilibrium, a discrepancy

between electron, ion and gas (neutral species) T_e , T_i , T_g appears. The temperature order of the species in non-thermal plasmas is as follows $T_e \gg T_i > T_g$, where T_g varies between room temperature and 10^3 K. The cold plasma is cheaper and easier to operate than the thermal plasma. However, the density of energized species is lower, thus, the conversion is lower than in the other plasma types. The examples of the non-thermal cold plasmas are dielectric barrier discharge (DBD), corona discharge, atmospheric pressure plasma jet (APPJ) and microwave plasma (MW) [52]. The summary is shown in Table 2-1. The major practical difference between the high temperature and cold plasma is the degree of reaction conversion, where the high temperature plasmas are more advantageous. On the other hand, the cost and handling complexity make the cold plasma a more attractive technology.

Table 2-1 Plasma classification [53] [54].

Plasma	Parameters	Example
Thermal equilibrium plasma or high temperature plasma	$T_e \approx T_i \approx T_g = 10^6\text{-}10^8$ K $n_e \geq 10^{20} \text{ m}^{-3}$ conversion – high Power _{consumption} ~MW	Fusion plasma, sun
Quasi-equilibrium plasma or warm plasma	$T_e \approx T_i \approx T_g \leq 2 \times 10^4$ K $n_e \geq 10^{20} \text{ m}^{-3}$	Plasma torch, arc plasma, RF induced plasma
Non-thermal equilibrium plasma or cold plasma	$T_e \gg T_i \approx T_g < 10^3$ K $n_e = 10^{10} \text{ m}^{-3}$ conversion – low P _{consumption} ~kW	Glow discharge plasma, DBD, MW, gliding arc

There follows a brief introduction to the gliding arc, microwave plasma and DBD plasma, which will be described in more detail in later chapters.

Figure 2-1 illustrates a generation of the gliding arc, where the high voltage is applied between the electrodes and an arc is created at the narrowest distance [54]. Since the gas is flowing between the electrodes, the arc “glides” in the flow direction. It moves until the voltage and current are sufficient to maintain the increased arc length, then the arc breaks and the new one is created again. The arc is itself at a very high temperature and possesses a large density

2. Theoretical background

of reactive ions and radicals, therefore, the gas flowing through the arc undergoes the chemical and electron impact reactions.

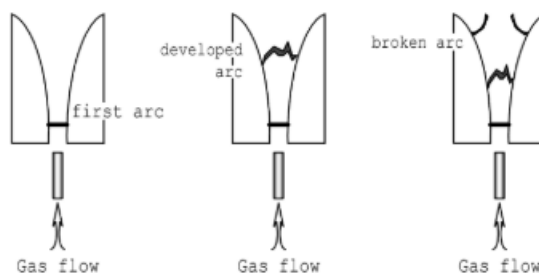


Figure 2-1 Gliding arc plasma development [54].

The scheme in Figure 2-1 has two main drawbacks. Firstly, the gas residence time within the arc is very brief. Secondly, a significant fraction of the gas flows around the arc in the reactor without being converted, leading to the energy waste [55]. To address these issues, a three-dimensional gliding arc reactor with the vortex flow, known as the gliding arc plasmatron (GAP), has been advanced, as seen in Figure 2-2. This GAP offers a higher conversion than the standard gliding arc and holds a great potential for the industrial application. Upon entering the reactor, the reverse-vortex mechanism directs the gas towards the center to the location of the arc. This effectively insulates the walls from convection heating, preventing the heat loss to the reactor walls or other parts, and ensuring that more energy is used by the discharge [56].

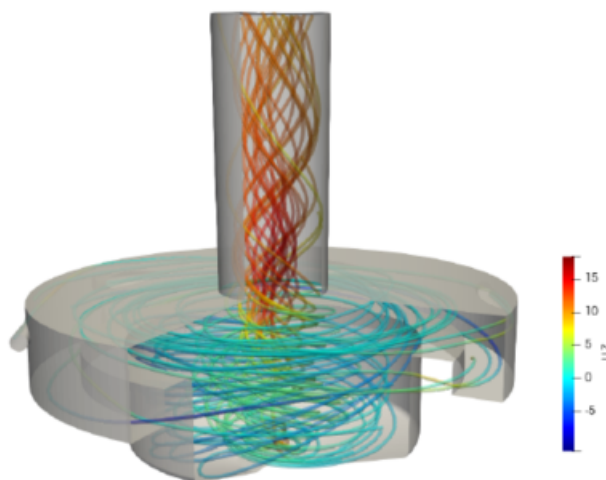


Figure 2-2 Gliding arc plasmatron with the reverse vortex flow, the colored scale represents the gas velocity.

The microwave plasma is obtained by electromagnetic waves at 2.45 GHz frequency, where plasma is sustained by the resulting local electric field. A typical schematic is given in Figure 2-3, where the reactant gas is introduced to the discharge tube, usually made of quartz. The

magnetron creates the electromagnetic waves, and the waveguide transmits the waves to the tube and generates the maximum electric field at the discharge tube. The electric field initiates the ionization reactions in the neutral gas, and hence, the conversion of the reactant gas into the product takes place [57]. The major products of CH_4 pyrolysis are H_2 , C_2H_2 , C_2H_4 .

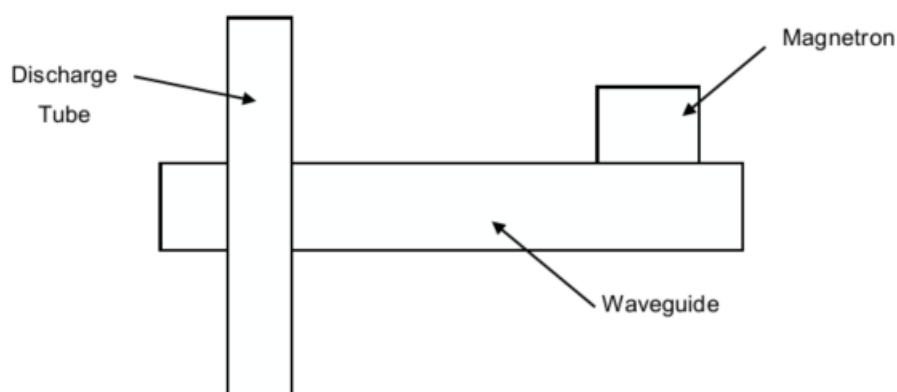


Figure 2-3 Schematic of microwave plasma reactor [58].

The dielectric barrier discharge (DBD) plasma is generated by the alternating current between two electrodes, of which at least one is insulated by a dielectric layer. This layer accumulates a charge on the surface but limits the current, so no spark is formed. Thus, a local electric field in the vicinity of electrodes gains its strength. The electric field then ionizes the gas and accelerates the species in the gas, creating the plasma. The setup is relatively easy to operate, however CH_4 conversion is relatively low. Experimental results indicate that the primary end products are H_2 and hydrocarbons of higher orders. Ethane (C_2H_6) is a major product among the formed hydrocarbons, with the selectivity between 20 % - 60 %, followed by other C2 molecules such as ethene (C_2H_4) and ethyne (C_2H_2), as well as C_3 - C_5 compounds and soot [59].

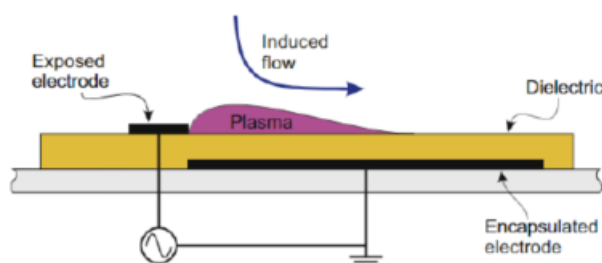


Figure 2-4 Surface barrier discharge plasma [60].

Figure 2-4 shows the schematic of the surface barrier discharge plasma (SDBD). SDBD reactor operates by applying a high-voltage alternating current or the pulsed power supply across the electrodes, which are separated by a dielectric material. The dielectric barrier

prevents the formation of a continuous arc, resulting in the generation of the non-thermal plasma. This plasma is composed of the reactive species such as ions, electrons, and radicals, which react with the incoming gas [61].

2.3 Modeling dimension classification

The plasma reactors can be represented in several modeling dimensions such as 0D, 1D, 2D and 3D, depending on the complexity of the reactors to be simulated. In this work, the plasma reactors are simulated following the bottom-up method. The plasma modeling begins with the 0D simulation, then it is extrapolated to 2D and finally the 3D plasma reactor model is obtained. The explanation of each step of such modeling strategy is given further.

The zero-dimensional (0D) plasma model is a simplified modeling approach that focuses on the reaction kinetics and plasma physics without considering the spatial variations [62]. The 0D model predicts the time evolution of the reactive species, radicals, electrons and ions, based on the calculated reaction rates without the added complexity of the reactor geometry dependencies [63]. The simplified nature of the 0D plasma enables a quick identification of the reaction pathways, which is a vital step for the reduction of the computational time in the more complex 2D and 3D plasma models. Since the reactive nature of the plasma may include thousands of the reactions, the selection of the reaction set can be performed by the 0D model [64]. Moreover, the operational parameters, namely the temperature, pressure, gas composition, flow rate and electrical discharge, can be evaluated in the 0D model [65] [66]. Therefore, the simulation domain in 0D must be chosen carefully, to represent the plasma correctly. In this work, the domain geometry was selected to coincide with dimensions of the plasma. For example, the arc images in the GAP reactor suggested that the plasma was in the shape of a cylindrical channel, with the radius of 200-300 μm and the length was equal to the whole distance between the anode and cathode. Figure 2-5 (left) is an example of the 0D model of the GAP reactor and the resulted dynamic simulation is depicted in Figure 2-5 (right). At first, the temperature, electric discharge and initial gas composition were homogeneous throughout the domain. Afterwards, a dynamic simulation was performed, where the change of the species could be observed as presented in Figure 2-5 (right).

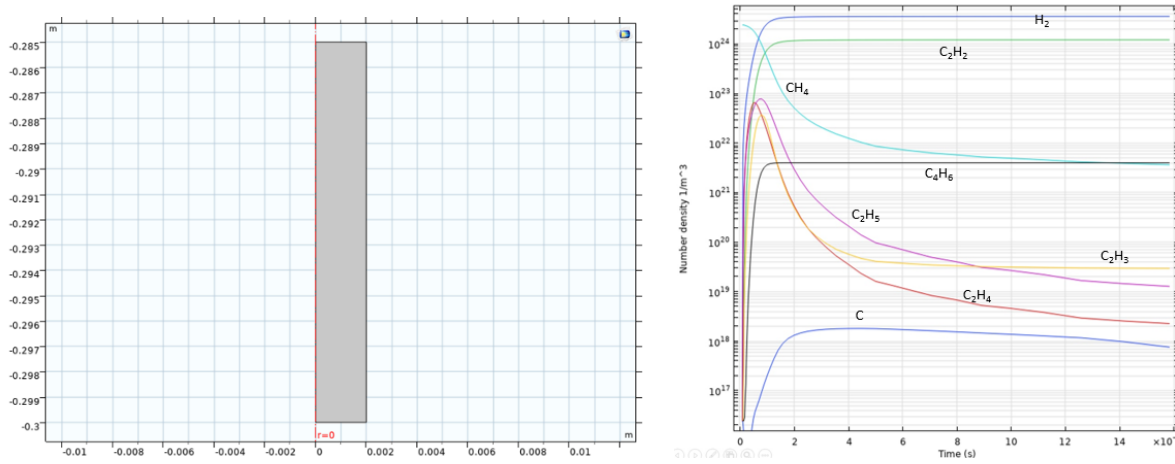


Figure 2-5 The 0D model domain (left) and the simulated temporal evolution of the species (right).

The graph presented in Figure 2-5 (right) can be compared to the experiments and literature, thus, giving the opportunity to tailor the reaction set and the operating conditions of the reactor. In the end, this enabled the optimization of the simulation effort in the next steps of 2D and 3D modeling.

The one-dimensional (1D) plasma model is a representation of the plasma reactor where the variations in the temperature, number density of species and electric field occur only along one axis in space [67]. In comparison to the 0D model, the 1D modeling approach is able to capture the heat and mass transport properties inside the plasma. Moreover, the 1D model is useful during the evaluation of the secondary plasma reactions, which are initiated by the vibrational excitation of the species and the quenching from the flowing gas [68]. Typically, the 1D plasma model is beneficial for the representation of the plasma reactors where the dominant physical and chemical processes appear along one axis. For instance, the inductively coupled plasma reactor during the etching process, plasma jet and dielectric barrier discharge plasma are the examples where the 1D model is sufficient to represent the necessary plasma phenomena. The assumptions that are necessary for the 1D model are the spatial symmetry, which allows one to neglect the variations in the other directions, the steady-state mode, which can be applied during the continuous plasma discharge, the negligible collision effects, which is applicable for the low pressure plasmas [69]. Figure 2-6 represents an example of the 1D model applied for the GAP reactor. The geometry was determined by the distance between the electrodes. The spatial profile in Figure 2-6 was captured after 10 ms, which was close to a residence time in the GAP reactor.

2. Theoretical background

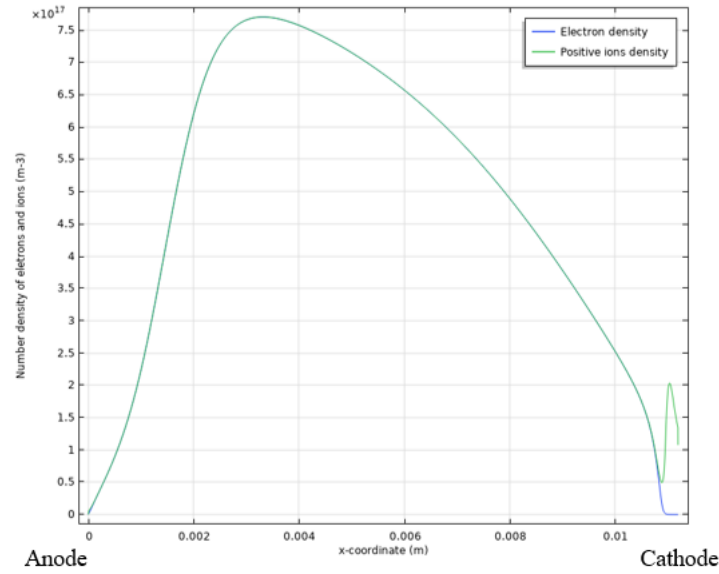


Figure 2-6 1D arc representation of the GAP plasma in terms of the electrons and ions density.

The sharp change of the ion density on the powered electrode side, which was in this case the cathode side, given in Figure 2-6 is the formation of the ion sheath. This phenomenon can occur due to the fact that the thermal velocity of the electrons is higher than that of the ions, hence, when the electrons drift away from the cathode, the ions accumulate on one electrode side. The ionic sheath formation cannot be seen in the 0D model, because all spatial variations are ignored [70]. Therefore, to observe the non-uniform electric field that impacts the ions and electrons interactions within the plasma environment, and to represent the dynamic behavior of the plasma charged particles in space, the 1D model is more enlightening than the 0D model. However, in this work, the 1D model was considered to be too limited, because of the nature of the studied plasma reactors. The examined GAP and MW plasma reactor geometries implied that the gas flew in the vortex, hence, much information would be lost if only 1D model was applied. Additionally, the SBDB plasma, which was investigated in this work, also indicated that the spatial variations were not only limited to one dimension. Thus, the 2D modeling technique was used in this work.

The two-dimensional (2D) plasma model is a more complex representation of the plasma behavior, where the variations of the variables, such as temperature, species density, electric field and gas velocity, are calculated across two dimensions in space [71]. The gas and plasma interactions can be portrayed in the axial and radial directions, or throughout the cross-sectional slice, depending on the geometry of the reactor. In this study, the 2D model portrayed the GAP, MW and SDBD plasma reactors through a cut plane view along the reactor axis in the Cartesian coordinates. In comparison to the 1D model, the 2D model provided a more realistic portrayal of the plasma dynamics. The simulation results from 2D were used for the

reactor design and operating conditions optimization, because these applied changes were instantaneously visible in 2D [71] [72]. However, one of the limitations of the 2D model was the increased computational effort compared to the 0D or 1D models. Additionally, the experimental validation was challenging due to the omission of third-dimensional information. Therefore, the advanced diagnostics methods, such as the optical emission spectroscopy, were essential to guarantee the correct selection of the 2D cut plane, making sure it accurately represented the entire reactor and did not overlook the significant plasma behavior. Figure 2-7 shows an example of how the optical emission spectroscopy was used to define the 2D model for the MW plasma.

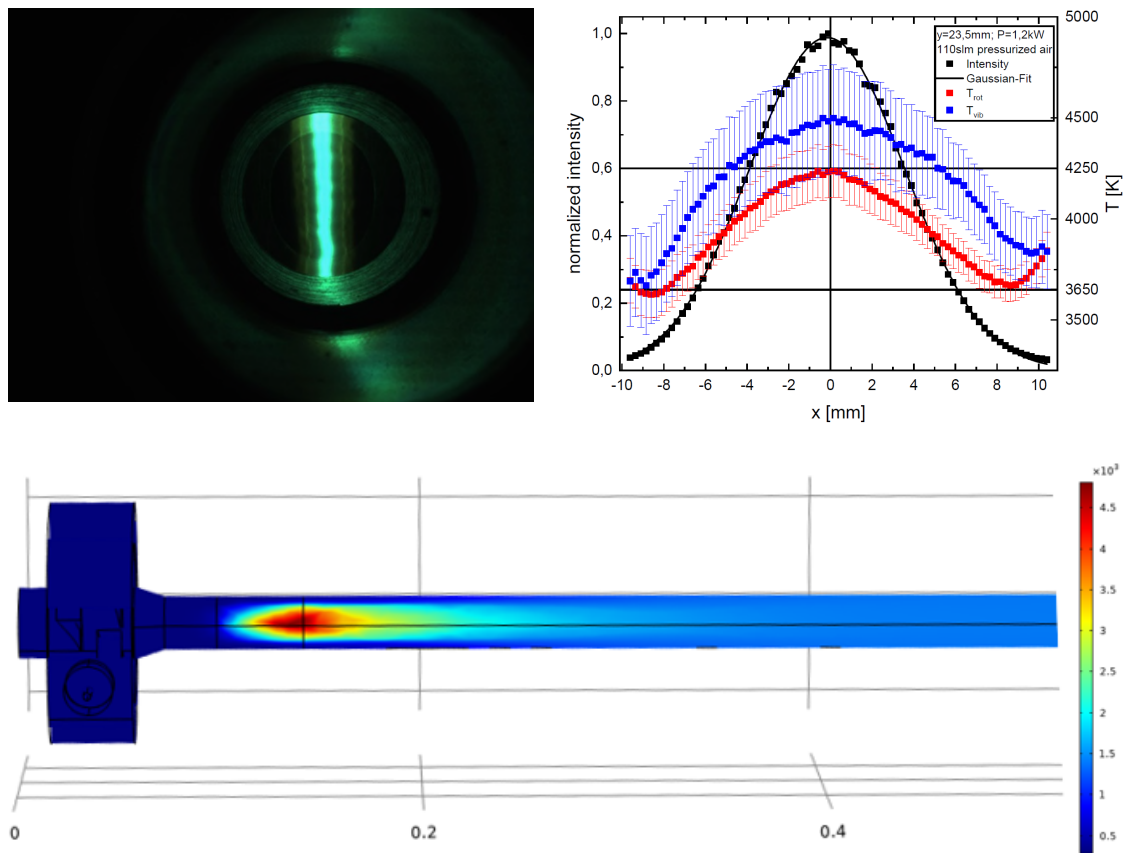


Figure 2-7 The representation of the optical analysis results to the 2D model [73].

The photo captured through the observation window and presented in Figure 2-7 evidenced the axial symmetry of the plasma, hence, making the 2D model applicable. The measured gas temperature from the optical emission spectroscopy indicated that the most significant variable changes in the gas temperature occurred in the radial and axial directions, while the changes in the third dimension were negligible. However, when comparing the experimental results in terms of the conversion and selectivities, some discrepancies between the simulation and reality were noticeable, which might stem from the simplifications made.

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The three-dimensional (3D) plasma model is an advanced methodology, which accurately represents the actual reactor geometry and the plasma dynamics. The 3D plasma model simulates the real-world scenarios more effectively than the simplified 0D and 2D models. This detailed representation leads to improved predictions of the species concentrations and energy distributions, aiding in optimizing the reactor conditions for the desired outputs [74]. However, the computational complexity of such numerical simulation requires high-performance computational power and longer simulation times [28]. The accuracy of the obtained simulation results is dependent on the modelling assumptions, the selected equations for the numerical solution and the representation of the plasma behavior. Including more details in the model makes it more realistic, but this comes at the cost of increased computational effort. This challenge can be addressed using artificial intelligence-based tools, which have seen increased use recently [75]. In this work, no machine learning techniques were applied, and the simulations were calculated by the numerical methods iteratively.

To develop the plasma reactor models within limited time and resources, a combination of 0D, 2D, and 3D models was used. For example, as shown in Figure 2-8, the 0D model results provided the initial values for the species concentrations. These values were then combined with the temperature and velocity profiles from the 2D model to obtain the concentration profile in 2D. This approach saved computational time and improved the convergence.

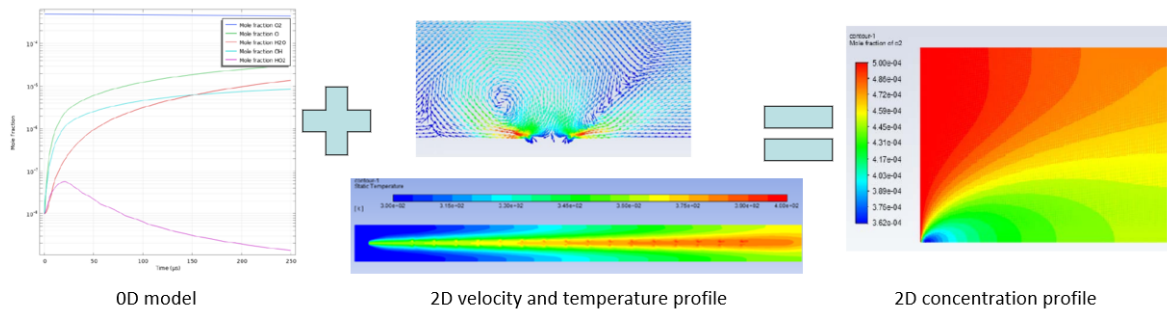


Figure 2-8 The combination of the 0D and 2D models.

The bottom-up strategy enabled the systematic development of the representative plasma reactor models. Initially, the 0D model was used to select the appropriate reaction set. Following this, the 3D model was simulated to analyze the fluid flow without incorporating the chemical reactions, which helped to identify the cut-out planes of interest for the 2D model. Subsequently, the 2D model was simulated and included a more complex plasma behavior. The insights gained from the 2D model regarding the reactor design and operating conditions were then tested in the 3D model. Finally, the 3D model results were validated through the experiments. These iterative steps were crucial for accurately simulating the plasma reactor, and the detailed results are presented and discussed in the subsequent sections.

2.4 Plasma Chemistry

Plasma chemistry is highly complex due to the multitude of the reactions occurring simultaneously. Broadly, there are two main types of the reaction mechanisms: the electron collision reactions and the thermally driven reactions. In the plasma, various electron collisions – both elastic and inelastic – generate numerous free radicals. These free radicals can recombine and participate in a variety of other radical reactions. Mainly there are following types of the electron impact reactions: attachment – when the electrons attach to the neutral species forming the negatively charged ions; elastic collisions – when the electrons collide with species without the energy transfer; ionization – when the electron leaves the molecule or atom resulting in the positively charged ion; excitation – when the electron impact raises an atom or molecule to the reactive energized state without producing the ion; dissociation – when the highly energized electrons break the molecule bonds leading to the creation of the radicals afterwards [76].

The product distribution varies with different plasma techniques and discharge conditions, making the plasma chemistry particularly suitable for the selective chemical synthesis. Thus, the plasma reactions are described separately for each plasma reactor. Table 2-2 gives a comparison between the reactors studied, regarding the methane conversion and product selectivity.

Table 2-2 Comparison of the methane pyrolysis in the plasma reactors.

Plasma reactor type	X_{CH_4} [%]	S_{H_2} [%]	$S_{C_2H_2}$ [%]	$S_{C_2H_4}$ [%]	$S_{C_2H_6}$ [%]
Gliding arc plasma [77]	40	35	45		
Microwave plasma [78]	43	25	61	11.5	
DBD plasma [79]	6-13	25	0.5	2	20-30

The conversion X_{CH_4} and product selectivity S_i are calculated by Equations (2-4) - (2-7):

$$X_{CH_4} = \frac{n_{CH_4} - n_{CH_4,0}}{n_{CH_4,0}} \quad (2-4)$$

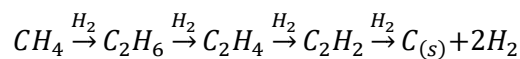
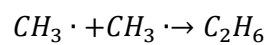
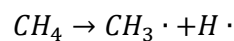
$$S_{C_2H_2} = 2 \frac{n_{C_2H_2}}{n_{CH_4} - n_{CH_4,0}} \quad (2-5)$$

$$S_{C_2H_4} = 2 \frac{n_{C_2H_4}}{n_{CH_4} - n_{CH_4,0}} \quad (2-6)$$

$$S_{H_2} = \frac{n_{H_2}}{2(n_{CH_4} - n_{CH_4,0})} \quad (2-7)$$

2.4.1 Chemistry in GAP

In the arc discharge, the mixture of the neutral and ionic substances is in the thermal equilibrium. At the temperatures exceeding 4000 K, the reactivity of ions is much lower than that of the neutral species [80]. Therefore, methane is mainly decomposed by the thermal effects, because the high temperatures supply sufficient energy for the activation of the dehydrogenation reaction. The reaction follows the Kassel mechanism: first methyl radicals ($\text{CH}_3\cdot$), which are generated by the dehydrogenation of methane, are recombined to ethane. Afterwards, the dehydrogenation reactions to ethene (reaction times 10^{-6} - 10^{-5} s), ethyne (reaction times 10^{-4} - 10^{-3} s) and finally to carbon soot and hydrogen occur:



The reaction chain indicates that the final products of the methane pyrolysis are carbon and hydrogen. Nonetheless, at the certain conditions (around 1500 K or lower), ethyne is generated from the methane pyrolysis at a faster rate than it decomposes to hydrogen. Thus, when the short residence times are applied (10^{-3} s) and efficient quenching is employed, ethyne can be formed as the main product [48].

Under the non-thermal plasma conditions the conversion of CH_4 is initiated by the electron impact reactions, and further reactions then occur between the free radicals and hydrocarbons formed. The electrons accelerate in the plasma due to the electric or magnetic fields, and thus, gain the kinetic energy. To determine the reaction rate coefficients, which are dependent on the electrical field, it is crucial to define the electron energy distribution function (EEDF), which is a probability density for the electron to acquire the energy [81]. Accurately obtaining a representative EEDF within a plasma reactor necessitates conducting the spatially dependent kinetic simulations, which can involve either treating the electrons as the discrete particles or solving the Boltzmann equation [82]:

$$\frac{\partial f(\varepsilon)}{\partial t} + \mathbf{u} \cdot \nabla f(\varepsilon) - \frac{\vec{e}}{m_e} (E \cdot \nabla_{\mathbf{u}} f(\varepsilon)) = C(f(\varepsilon)) \quad (2-8)$$

where $f(\varepsilon)$ – distribution function, $\mathbf{u}$ – velocity vector, $\vec{e}$ – electron charge, m_e – electron mass, E – electric field, $C(f(\varepsilon))$ – rate of change of energy distribution function due to collisions [82].

Equation (2-8) can be expanded by the two-term approximation – isotropic and anisotropic components, where the isotropic term includes particle and energy balance, and the anisotropic term includes the influence from the electric field and charge particle density

gradient that impacts the transport direction of the charged species [82]. Thus, Equation (2-8) becomes (2-9):

$$-\frac{d}{d(\varepsilon)} \left[\frac{\vec{E} \varepsilon}{n_0} \frac{1}{3} f^1(\varepsilon) \right] = \frac{1}{n_0} \sqrt{\frac{m_e \varepsilon}{2}} \left(\frac{\partial f(\varepsilon)}{\partial t} \right) \equiv C(f(\varepsilon)) \quad (2-9)$$

$$f^1(\varepsilon) = \frac{\vec{E}}{n_0} \frac{1}{\sigma_m(\varepsilon)} \frac{\partial f^0(\varepsilon)}{\partial \varepsilon}$$

where n_0 – ground-state density of the neutral molecule, σ_m – momentum transfer cross section, and $C(f(\varepsilon))$ expressions are given in Appendix ((9-1) - (9-4)).

This approach ensures the comprehensive integration of the plasma parameters – such as the dissociation levels and the ionization percentages – with the electrodynamics into the kinetic calculations; however, these techniques tend to be computationally demanding.

An alternative methodology for addressing the electron kinetics involves assuming a predetermined EEDF such as the Maxwellian distribution.

$$f(\varepsilon) = \varepsilon_k^{-3/2} \beta_1 \exp\left(-\frac{\varepsilon \beta_2}{\varepsilon_k}\right) \quad (2-10)$$

$$\beta_1 = \Gamma(5/2)^{3/2} \Gamma(3/2)^{-5/2}, \beta_2 = \Gamma(5/2) \Gamma(3/2)^{-1}$$

where, $\varepsilon_k = (3/2)k_B T_e$ – mean electron energy, Γ – incomplete Gamma function [82].

The Maxwellian model presumes the stable equilibrium states while disregarding any influence from the inelastic collisions on this distribution function. When employing a Maxwellian EEDF, one derives the reaction-rate coefficient for the particular reactions through the integration involving the factors such as the collision cross sections related to the electron energy dependence, along with the constants including the electron mass and mean temperature based on the Boltzmann's constant, as shown in Equation (2-11):

$$k_j(T_e) = \left(\frac{8}{\pi m_e}\right)^{1/2} \left(\frac{1}{k_B T_e}\right)^{3/2} \int_0^\infty \varepsilon \sigma_j(\varepsilon) e^{-\frac{\varepsilon}{k_B T_e}} d\varepsilon \quad (2-11)$$

where k_j is the reaction rate constant for j reaction as a function of T_e , m_e is the electron mass. The collision cross section data $\sigma_j(\varepsilon)$ used in the integration is obtained from the literature [83].

In some literature the methane discharge EEDF aligns more closely with a Druyvesteyn distribution rather than the Maxwellian distribution [84]:

$$f(\varepsilon) = \varepsilon_k^{-3/2} \beta_1 \exp\left(-\left(\frac{\varepsilon \beta_2}{\varepsilon_k}\right)^2\right) \quad (2-12)$$

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$$\beta_1 = \Gamma\left(\frac{5}{4}\right)^{3/2} \Gamma\left(\frac{3}{4}\right)^{-5/2}, \beta_2 = \Gamma\left(\frac{5}{4}\right) \Gamma\left(\frac{3}{4}\right)^{-1}$$

However, the Druyvesteyn distribution is accurate only for the low ionization degree plasmas, where the elastic collisions of the electrons are dominant, and the inelastic collisions are insignificant. Also, for a more accurate representation a Boltzmann distribution function can be applied. The Boltzmann form depicts the EEDF at a low and high energy with a greater precision as presented in Figure 2-9.

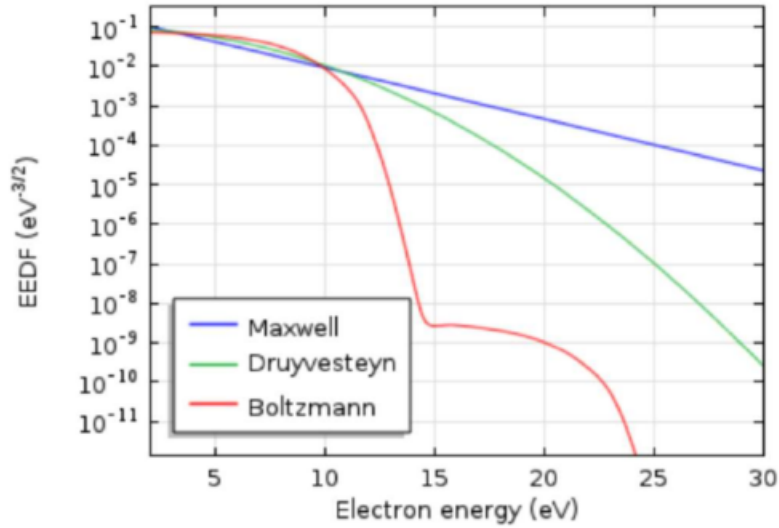


Figure 2-9 Energy distribution functions comparison: Maxwell, Druyvesteyn, Boltzman [84].

Among these EEDFs, the Maxwell distribution is the least computationally challenging and the fastest to converge. Considering the complexity of the plasma modeling and the large set of reactions in the plasma, it was decided to proceed with using the Maxwellian EEDF.

For calculating the reaction-rate coefficients from the collision cross section data, an open-source software BOLSIG+ was used [85]. A list of the electron impact reactions used in the simulation is given in the Appendix. The results from the BOLSIG+ software, for varying the electric field and electron energy, yield the reaction-rate coefficients in a type of the Arrhenius equation. Assuming that the electron temperature T_e and the gas temperature T_g are equal in plasma, the reaction rate constant can be described by Equation (2-13):

$$k_j(T_e) = A_j T_g^n \exp\left(-\frac{E_{a,j}}{RT_g}\right) \quad (2-13)$$

where A_j – the frequency factor, $E_{a,j}$ – the activation energy as calculated by BOLSIG+ based on the cross sectional data.

During the conversion of methane in plasma, the methane molecules are initially dissociated through the direct electron impact reactions to produce various free radicals such as $\text{CH}_3\cdot$, $\text{CH}_2\cdot$, and $\text{CH}\cdot$ [86]:



These generated radicals can then recombine and undergo a variety of additional radical reactions. They, thus, form the by-products ethane, ethene and ethyne.

The reaction pathway was summarized by [81] using the following schematic given in Figure 2-10. The box sizes in Figure 2-10 are proportional to the species concentrations. Therefore, it is visually clear which species prevail, and which are the intermediate reactants. The arrows between the species in Figure 2-10 indicate the different types of reactions in which these species are involved. Hence, it is evident that the species are constantly consumed and produced by the various reactions.

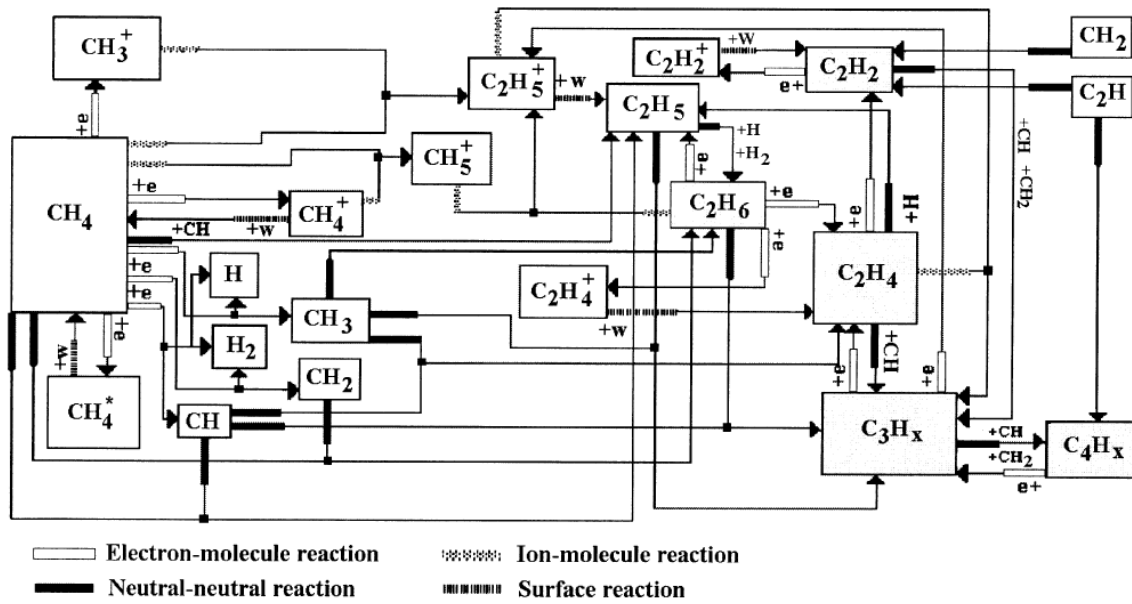


Figure 2-10 Schematic pathway of reactions [81].

In some cases, to increase the plasma efficiency, an additional plasma gas, for instance, Argon, is introduced into the system. Ar is an inert gas, which easily ionizes and stabilizes plasma. Ar plasma reactions are given in Table 2-3. Ar plasma is easier to sustain than the CH_4 plasma. The addition of Ar to CH_4 is advantageous, due to its ability to stabilize and maintain the plasma discharge. For instance, an increase in the argon composition in the gas mixture results in the enhanced electron density, which significantly contributes to the effective

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dissociation of the methane molecules into the reactive species [87]. The presence of argon enhances the ionization efficiency, which contributes to the improved energy transfer within the plasma environment and increases the methane conversion [88]. To simulate $\text{CH}_4 + \text{Ar}$ plasma reactions, Ar related electron impact reactions were added to the previously described methane reactions [89]:

Table 2-3 Ar electron impact reactions [89].

Reaction	Type of electron impact reaction	Threshold energy (eV)
$e + \text{Ar} \rightarrow e + \text{Ar}$	Elastic	-
$e + \text{Ar} \rightarrow e + \text{Ar}^s$	Excitation	11.5
$e + \text{Ar}^s \rightarrow e + \text{Ar}$	Elastic	-
$e + \text{Ar} \rightarrow 2e + \text{Ar}^+$	Ionization	15.8
$e + \text{Ar}^s \rightarrow 2e + \text{Ar}^+$	Ionization	4.24
$\text{Ar}^s + \text{Ar}^s \rightarrow 2e + \text{Ar} + \text{Ar}^+$	Ionization	-
$\text{Ar}^s \rightarrow \text{Ar}$	Surface reaction	-
$\text{Ar}^+ \rightarrow \text{Ar}(\text{wall})^+$	Surface reaction	-

Figure 2-11 represents how excited Ar species accelerate the CH_4 conversion [90]. Ar ions and electrons from the Ar plasma react with the neutral CH_4 molecules, and produce CH_3 , CH_2 , CH radicals and ions. These reactive species are then converted to hydrogen, and other byproducts.

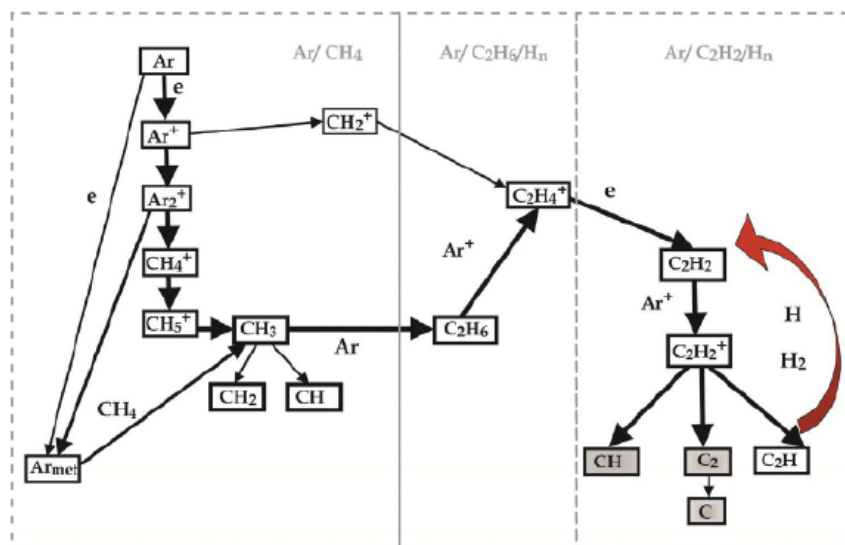


Figure 2-11 $\text{CH}_4 + \text{Ar}$ plasma reaction pathways [90].

The introduction of other plasma carrier gases was considered as well, and the results are presented in the further sections.

2.4.2 Chemistry in MW-Plasma

The modeling and simulation of the microwave plasma systems, a field that has seen significant development since its initial efforts in the 1990s, presents the unique challenges. Early attempts examined the reactions between methane and nitrogen in a low-pressure microwave plasma [91]. This work, which involved varying the flow rates and the methane inlet concentrations, utilized a 2.45 GHz microwave generator paired with a waveguide cavity to create the plasma within a silica tube. The stable species concentrations were analyzed through the gas chromatography at the various points inside the tube, identifying methane, N_2 , H_2 , and hydrocarbons such as C_2H_y , notably C_2H_2 as the primary products. A gas temperature ranging from 300 to 800 K was recorded during these experiments using a thermocouple. Additionally, the electron density and electron temperature measurements were obtained using a floating probe positioned near the plasma region. Based on these experimental findings, a one-dimensional model comprising 24 species and 61 reactions was developed, representing the electrons, hydrocarbons, radicals, hydrogen, and nitrogen compounds while excluding the ions due to their minimal presence in the data collected. The reactions considered included the ion dissociation via the electron impact and the dissociation by the excited nitrogen species alongside the two- and three-body reactions involving the hydrocarbons and atomic nitrogen. By disregarding the particle diffusion and the drift effects, the reaction rates were adjusted to model both the time- and spatially-dependent concentration changes of the 24 species involved. This model facilitated an investigation into the initial CH_4 dissociation process; it was determined that the variations in the electron quantities had the negligible effects on the methane dissociation since the resulting concentrations remained significantly lower than those observed experimentally [91] [92].

Continuing with the similar methodologies combining the experimental work with the subsequent modeling efforts, some researchers explored the methane conversion enhanced by the hydrogen addition for the ethyne production within the microwave plasma environments [93]. Pulsed microwaves generated plasma from pure CH_4 under the low pressure conditions; the products were analyzed through the chromatography revealing up to 90 % conversion that correlated linearly with the input power while the selectivity towards C_2H_2 reached 80 %. The supplementary optical emission spectroscopy provided the real-time diagnostics of the plasma area enabling the detection of the CH_3 , CH_2 , CH , and H species. The qualitative assessments based on the measured intensity levels allowed for the further exploration of the reaction mechanisms where the rate-limiting step identified was the CH_4 dissociation yielding the H radicals; other reaction steps occurred rapidly analogous to the thermal processes. This led

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to the identification of 2 groups of reactions for the methane conversion. One set of the reactions includes the dehydrogenation reactions of C_1 and C_2 species by the H radical. Whereas the second group of the reactions are the dimerization of the formed radicals [93].

Having argon as a plasma carrier gas requires a more thorough consideration, thus a model describing argon microwave plasma (operating at 2.45 GHz) under the atmospheric pressure exists [94]. Despite its simplicity involving just 5 species and 14 reactions relative to the other models - the uniqueness lies in its fully coupled two-dimensional simulation addressing the momentum alongside the energy balances which aligned well with the experimental data observed at the flow rates between 0.2 – 0.4 l/min coupled with an input power of 20 W where the maximum gas temperatures reached were approximately 2100 K.

There are zero- and one-dimensional models described in the literature for the MW plasma, structured around 20 species corresponding to 48 chemical reactions derived from the mechanisms of methane oxidation at the high-temperature under constant pressure [95]. Whilst ignoring the ions or the excited states due assumed insufficient energy levels, inhibiting the direct ionization processes leading to the simulations indicating that the methane conversion initiates at the temperatures around 1200 K. It was simulated that nearly the complete conversion at ca. 4000 K was reached, with the primary pyrolysis products being H_2 alongside C_2H_2 and C_2H_4 emphasizing the thermally driven kinetics.

Later, the simulation and modeling research on the MW plasma included 57 species, comprising from the radicals, ions, excited states and higher hydrocarbons as C_3H_x/C_4H_y , and 2174 reactions [96]. Comparing the 0D modeling and the experiments demonstrated that the CH_4 conversion was dependent mainly on the thermal profiles, influenced by the energy input from plasma, potentially achieving up to 100% conversion for the certain operating conditions. In the context of the microwave plasma at the atmospheric pressure, the key reactions involving CH_4 , CH_3 , C_2H_6 , C_2H_5 , C_2H_4 , C_2H_3 , C_2H_2 , and C_2H were highlighted, with ethyne identified as the primary product. A comparison was made between a comprehensive reaction mechanism and a simplified version that omits the electron-impact reactions, which did not account for the ion or excited species formation. At the elevated temperatures exceeding 2000 K, the thermal reactions governed the chemistry, resulting in the similar conversions for both the reduced and complete mechanisms. For the high-temperature plasma systems that attain the temperatures above 3000 K - such as the atmospheric microwave reactors, the methane conversion process is, therefore, primarily thermal.

Table 2-4 summarizes all of the above mentioned MW plasma kinetics.

Table 2-4 Overview of MW plasma kinetics modeling.

Reactants	No. species and reactions	Operating pressure	Model dimension	Reference
CH ₄ , N ₂	24 species, 61 reactions	low p	1D	[91]
CH ₄ , H ₂	12 species, 19 reactions	low p	0D	[93]
C ₂ H ₂ , H ₂ , Ar	26 species, 73 reactions	low p	0D	[97]
Ar	5 species, 14 reactions	atmospheric	2D	[94]
CH ₄	20 species, 48 reactions	atmospheric	0D, 1D	[95]
CH ₄	57 species, 2174 reactions	atmospheric	0D	[96]

These kinetic data were used for the MW plasma simulation, and the most suitable reaction set was selected. This will be discussed in the subsequent sections of this work.

2.4.3 Chemistry in SDBD-plasma

The SDBD plasma simulated in this work, unlike the GAP and MW plasma, did not involve CH₄ as a reactant. The experimental results were performed with H₂, O₂ and N₂. Although, the SDBD plasma was not utilized for the methane pyrolysis, simulating SDBD with simpler molecules helped to understand the plasma simulation better and prepared the foundation for future applications, in which methane could be introduced in the system.

The plasma-chemical reactions involving H₂, O₂, and N₂ were examined both individually and as the combinations of two or three species, to explore the formation of the unstable and highly reactive radicals and the metastable species. The research on the plasma-assisted combustion reactions has been conducted extensively to improve the kinetic aspects of the combustion process, which has applications in the jet propulsion [98] [99]. The plasma-assisted oxidation of hydrogen was analyzed as an initial step towards comprehending the intricate hydrocarbon combustion systems. In the literature, experiments on hydrogen

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oxidation within an $\text{H}_2/\text{N}_2/\text{O}_2$ mixture at atmospheric pressure, using pulsed surface dielectric barrier discharge (SDBD), were described based on the reaction mechanism for H_2/O_2 combustion [100] [101]. The H_2/O_2 conversion was reported as high as 99 % and the exhaust gas temperature reached 80 °C [100]. In some cases, the reactions with HO_2 played a significant role in the O, H, and OH radicals' consumption and generation, and as a result on the hydrogen oxidation [99].

The experimental results with H_2 , O_2 , and N_2 on the packed bed DBD reactor showed that H_2O was formed without the NH_3 and NO_x formation. Hence, it was assumed that there is no reaction between H_2 and N_2 or O_2 and N_2 . Therefore, the reactions set was reduced to the elementary reactions with the H and O atoms and their derivatives: H, O, OH, H_2O , HO_2 , H_2 , O_2 , and H_2O_2 [102]. It is worth noting that the O_2 conversion was raised from 30 to 80 % when the packed bed was assisted with the DBD plasma [102].

When the electron-impact reactions were included, the system contained 141 reactions that involved 21 different species [103] [100] [101]. The species involved are listed in Table 2-5, and the reactions are given in Appendix (Table 9-8, Table 9-9, Table 9-10).

Table 2-5 Plasma species included for simulation.

Neutral species	H, O, OH, H_2O , HO_2 , H_2O_2 , O_2 , H_2 , O_3
Charged species	H^+ , O^+ , O_2^+ , OH^+ , H_2O^+ , H_2^+ , H_3O^+ , HO_2^+ , OH^- , H^-
Metastable species	$\text{O}^1(\text{D})$, $\text{O}_2(\text{a})$

The simulation results, which utilize the discussed reaction kinetics will be discussed later in this work.

2.5 Fluid flow model

To successfully simulate the fluid flow and heat transport, it is necessary to first establish a theoretical foundation. The various models and simplifications were applied in this process. The characteristics of the flow – whether it is compressible or incompressible, and whether it is turbulent or laminar – depend not only on the geometry but also significantly on the thermodynamic properties of the fluid, flow conditions and the operating conditions.

This subsection explains the fundamental equations of fluid mechanics and their relationship to the thermodynamics. Additionally, it discusses the implementation of these models in the simulation software and presents the calculations that validate the decisions regarding the chosen models and simplifications within the simulation.

2.5.1 Ideal Gas law

To simplify the calculations the flowing gas can be considered as an ideal gas. Generally, the gases can be described as the ideal gases if their state variables are far from the critical point during the observation. This means that a pressure is well below the critical pressure, and the temperature is well above the critical temperature. Often, a significant exceedance of the boiling temperature is also used as a criterion, although this criterion is weaker than that the critical point. Some properties of the pure gases such as argon, carbon dioxide, nitrogen, as well as the averaged values for air, are listed in Table 2-6. This choice of the gases is not random. These are the typical plasma carrier gases used for methane pyrolysis in plasma.

Table 2-6 Thermodynamic properties of Ar [104], CO₂ [105], N₂ [106], Air [107], CH₄ [108].

Property	Ar	CO ₂	N ₂	Air	CH ₄
p_{crit} [Pa]	48.98x10 ⁵	73.8x10 ⁵	36.0x10 ⁵	37.2x10 ⁵	46.1x10 ⁵
T_{crit} [K]	150.9	304.2	126.1	132.5	190.6
ρ_{crit} [mol/l]	13.4	10.6	11.2	11.2	10.1
T_{boil} [K]	87.3	-	77.4	80.2	111.2
F – factor	3	≈7	5	≈5	≈15

The standard ambient temperatures encountered in the plasma reactors are 300 K or above, and usually the pressure is equal to the atmospheric conditions, approximately 1.013×10^5 Pa. Therefore, the gases argon, nitrogen, methane, and air could be treated as the ideal gases under these conditions. For carbon dioxide, this assumption is no longer readily applicable, as the critical temperature of 304.2 K is close to the ambient temperature.

For the ideal gases, the state variables can be determined using the state equations. In their classical molar form, the equation of state connects the temperature T , pressure p , volume V , and number of moles n , while the caloric state equation connects the internal energy E , n , and T . The relations are given in Equations (2-17) - (2-19):

$$pV = nRT \quad (2-17)$$

$$E = nC_V T \quad (2-18)$$

$$H = E + pV = nC_p T \quad (2-19)$$

2. Theoretical background

In the later sections the fluid flow and the Navier-Stokes equation used for the simulation will be explained in detail. In the equations mentioned here, the internal energy e and enthalpy h , as well as the constants c_p , c_v and R_{spec} are mass specific.

$$p = \rho \frac{R}{M} T = \rho R_{spec} T \quad (2-20)$$

$$e = c_v T \quad (2-21)$$

$$h = e + p \frac{V}{m} = e + \frac{p}{\rho} \quad (2-22)$$

Hence, the temperature is calculated from the internal energy e and the specific heat capacity at constant volume c_v , or through the enthalpy h and the specific heat capacity at the constant system pressure c_p :

$$T = \frac{h}{c_p} = \frac{e}{c_v} \quad (2-23)$$

For the ideal gasses c_v and c_p , or C_p and C_v , can be obtained from the gas constant and the F factor.

$$c_v = \frac{C_v}{M} = R_{spec} \frac{F}{2}, c_p = \frac{C_p}{M} = R_{spec} \frac{F+2}{F} \quad (2-24)$$

The factor F (degrees of freedom) is fundamentally dependent on the molecular structure of the gas molecules and the temperature. For the gas molecules with only one atom that are well above their boiling point, $F = 3$. This is the case for all noble gases, including argon considered here. Thus, for the monatomic gases, $C_v = 3/2R$ and $C_p = 5/2R$. For the gas molecules with two atoms, $F = 5$ over a wide range of temperatures. Therefore, for a gas mixture like air, which to 98 % consists of the diatomic gases nitrogen and oxygen, $F = 5$ can be assumed. For such gases, $C_v = 5/2R$ and $C_p = 7/2R$. The mass-specific values are calculated as in the previous equations by dividing by M. However, it should be noted that for the gases with more than two atoms, such as methane or carbon dioxide, C_p and C_v are strongly temperature-dependent, as their degrees of freedom increase with the temperature. To illustrate this, Figure 2-12 shows the temperature-dependent C_p values for the gases argon, air, methane, and carbon dioxide.

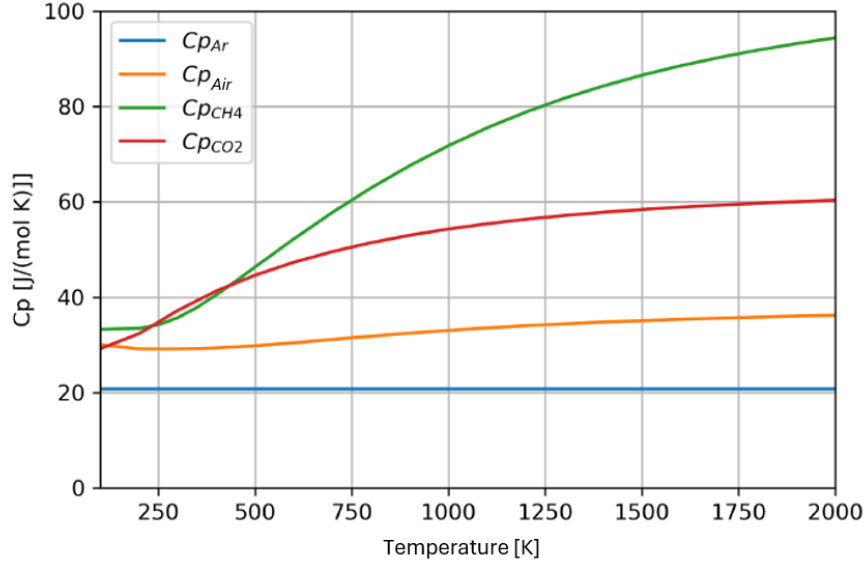


Figure 2-12 Temperature dependency of C_p [J/mol K] for Ar [109], Air [107], CH_4 [109] and CO_2 [109].

As picture in Figure 2-12, C_p for argon remains constant over the entire temperature range, and C_p for carbon dioxide continuously increases over along the temperature increase. And for methane, C_p increases after 250 K. The temperature dependence for air is not as pronounced; however, the relative increase in C_p from 300 K to 2000 K is just 24 %.

In the simulation of a plasma, very high local temperature differences of over 1000 K occur, which can have a significant impact on C_p . Therefore, for the polyatomic gases such as air, methane, or carbon dioxide, either the enthalpy tables or interpolating functions for $C_p(T)$ such as the NASA polynomials should be implemented [110]:

$$C_p = R \times (a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4) \quad (2-25)$$

The diffusion coefficient, based on Ar as the main component, is given by Equation (2-26) [111]:

$$D_{i,Ar} = 2.66 \times 10^{-22} \sqrt{\frac{T^3 \frac{M_i + M_{Ar}}{2 \times 10^3 M_i M_{Ar}}}{\rho \sigma_i \sigma_{Ar} \Omega^{(1,1)*}}} \quad (2-26)$$

where M is the molar mass, σ_i is the characteristic potential length, $\Omega^{(1,1)*}$ is the collision integral calculated by Equation (2-27) [112].

2. Theoretical background

$$\begin{aligned}\Omega^{(1,1)*} = & 1.064 \left(\frac{T}{\varepsilon_k} \right)^{-0.156} + 0.193 \left(\exp \left(\frac{-0.476T}{\varepsilon_k} \right) \right) + 1.036 \left(\exp \left(\frac{-1.53T}{\varepsilon_k} \right) \right) \\ & + 1.765 \left(\exp \left(\frac{-3.894T}{\varepsilon_k} \right) \right) + \frac{4.75 \times 10^{-40} \mu_{D,i}^2 \mu_{D,Ar}^2}{K^2 T \varepsilon_k \sigma_i^3 \sigma_{Ar}^3}\end{aligned}\quad (2-27)$$

$$\text{where } \varepsilon_k = \sqrt{\frac{\varepsilon_i \varepsilon_{Ar}}{k_b^2}}$$

and μ_D is the dipole moment, ε_i is the minimum potential energy.

The dynamic viscosity can be calculated as follows:

$$\mu_i = 2.67 \times 10^{-6} \frac{\sqrt{T \cdot M_i 10^3}}{\sigma_i^2 \Omega^{(2,2)*}} \quad (2-28)$$

where the collision integral is obtained in a similar way:

$$\begin{aligned}\Omega^{(2,2)*} = & 1.161 \left(\frac{T}{\varepsilon_k} \right)^{-0.149} + 0.525 \left(\exp \left(\frac{-0.773T}{\varepsilon_k} \right) \right) + 2.162 \left(\exp \left(\frac{-2.438T}{\varepsilon_k} \right) \right) \\ & + \frac{4.99 \times 10^{-40} \mu_{D,i}^2}{k_b T \varepsilon_i \sigma_i^6}\end{aligned}\quad (2-29)$$

And the viscosity of the gas mix of n – number of species is based on the molar fraction x_i and the dynamic viscosity of each species, together with the aid of the dimensionless variable ϕ_{ij} [112]:

$$\mu = \sum_{i=1}^n \left(\frac{\mu_i}{1 + \frac{1}{x_i}} \times \frac{1}{\sum_{j=1(j \neq i)}^n x_j \phi_{ij}} \right) \quad (2-30)$$

$$\phi_{ij} = \frac{\left(1 + \left(\frac{\mu_i}{\mu_j} \right)^{0.5} \left(\frac{M_j}{M_i} \right)^{0.25} \right)^2}{2 \sqrt{2 \left(1 + \frac{M_j}{M_i} \right)}} \quad (2-31)$$

The thermal conductivity of each species i , k_i , is calculated by the empirical Equation (2-32) [113], and the thermal conductivity of the mix is given in Equation (2-33) [114]:

$$k_i = \frac{\mu_i}{M_i} (1.15 \times C_p + 0.88 \times R) \quad (2-32)$$

$$k = \left(\sum_i^n \frac{x_i k_i}{\sum_j^n x_j \phi_{ij}} \right) \quad (2-33)$$

The equations described above were used to predict the gas changes influenced by the temperature, pressure and gas content.

2.5.2 Fluid dynamics modeling

The fluid dynamics is a fundamental branch of physics and engineering that examines the behavior of the fluids - encompassing both liquids and gases - in motion. It constitutes a sub-discipline of the fluid mechanics, which also includes the fluid statics, the study of the fluids at rest. The principles of the fluid dynamics are applied across diverse fields, including meteorology, oceanography, engineering, biology, and even astrophysics [115]. At its core, the fluid dynamics examines the forces and energy transfers that govern the motion of the fluids, employing the mathematical principles to describe these behaviors. This section provides the theoretical background behind the fluid flow simulation of the plasma reactors.

The fluid dynamics revolves around several key principles and equations that govern the behavior of the fluids in motion. The conservation laws in the fluid dynamics are the fundamental principles that govern the interaction of the various physical quantities within a fluid system. These laws are derived from the principles of mass, momentum, and energy conservation, which are integral to the mathematical modeling of the fluid flows. In essence, the conservation laws dictate that the specific physical quantities remain constant throughout the motion of fluids, allowing for a coherent understanding of the fluid behavior and its dynamics across the various applications.

The law of conservation of mass, often represented by the continuity equation, asserts that the mass in a closed system remains constant over time. Mathematically, this is expressed through the continuity equation, which balances the influx and outflux of the mass within a given control volume [116]. Through several approaches, researchers have established that these laws encompass not only the mass but also momentum and energy [117]. In the fluid dynamics, the momentum conservation law is typically represented by the Navier-Stokes equations, which articulate the relationship between the velocity, pressure, density, and external forces acting on the fluid [118]. The conservation of energy is based on the principle that the energy of the closed system is constant [119].

The continuity (2-34), Navier-Stokes (2-35) and energy (2-36) equations are as follows:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (2-34)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \cdot \nabla^2 \mathbf{u} + \mathbf{f} \quad (2-35)$$

$$\rho \left(\frac{\partial \varepsilon}{\partial t} + \mathbf{u} \cdot \nabla \varepsilon \right) - \nabla \cdot (K_H \nabla T) + p \nabla \cdot \mathbf{u} = 0 \quad (2-36)$$

2. Theoretical background

where $\mathbf{u} = (u, v, w)$ is a velocity vector in Cartesian coordinates (x, y, z) , ρ is the density, μ is the viscosity, t is time, p is the pressure, f are the body forces, ε is the internal energy, K_H is the heat conduction coefficient, T is the temperature.

The equations above are the coupled partial differential equations that can, in theory, be addressed through the calculus methods for the specific flow scenarios. However, the pursuit of analytical solutions to these equations poses considerable challenges in practice. Traditionally, different approximations and simplifications are applied to achieve a solvable form of the equations. In recent years, the advancements in high-speed computing have significantly enhanced the ability to solve these equations by utilizing a range of techniques, including the finite difference, finite volume, finite element, and the spectral methods. This field of study is commonly referred to as the Computational Fluid Dynamics (CFD).

To simulate the flow in the reactor correctly, firstly, it should be established if the flow is laminar or turbulent. The laminar and turbulent flows are two fundamental types of the fluid motion characterized by different flow patterns and behaviors. Figure 2-13 shows an exemplary difference between the laminar and turbulent flows. In the laminar flow the velocity gradient is uniform, whereas in the turbulent region the velocity gradient is unsteady.

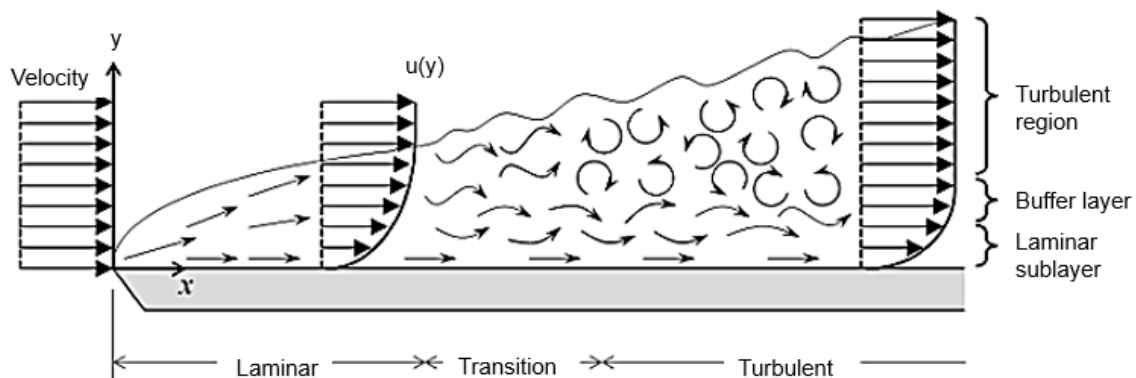


Figure 2-13 Laminar and turbulent flow patterns.

The laminar flow is characterized by smooth, orderly movement of the fluid particles along the well-defined streamlines, where the velocity at any point is constant and exhibits little to no mixing between the fluid layers. The flow generally remains stable and can be quantitatively characterized by the low Reynolds numbers (typically $Re < 2000$), indicating a predominance of the viscous forces over the inertial forces [120] [121]. Under such conditions, the individual fluid particles behave predictably, and the flow path follows a streamlined pattern, often resembling the layers that glide over one another [122]. The Reynolds number is usually calculated by the relation of the flow velocity u , the characteristic length d , and the viscosity of the fluid $\frac{\rho}{\mu}$:

$$Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho \cdot u \cdot d}{\mu} \quad (2-37)$$

In contrast, the turbulent flow is characterized by the chaotic changes in the pressure and velocity, leading to the irregular fluctuations and the mixing of the fluid layers. This occurs at the high Reynolds numbers (typically $Re > 4000$), where the inertial forces dominate over the viscous forces [121]. In the turbulent flow, the fluid particles experience random fluctuations resulting in the eddies and swirls, and substantial mixing is observed across the different layers of the fluid. This complexity in the motion poses challenges for the prediction and modeling as the flow becomes non-linear and inherently unpredictable [123].

To identify whether a flow is laminar or turbulent, additionally, the visual methods such as the flow visualization techniques (e.g., particle image velocimetry) and the coherent structures in the flow patterns could help to determine the flow characteristics, as the turbulent flows display more irregular and turbulent structures compared to the smooth, organized patterns of the laminar flow [124]. The experiments on the flows under varying conditions, such as the surfaces with roughness or the variations in geometry, also reveal transitions between the laminar and turbulent states, emphasizing the sensitivity of the flow behaviors to the external factors [121] [125].

The transitional flow regime, which occurs between the laminar and turbulent states, typically displays the characteristics of both types of flow, containing the regions where the laminar and turbulent features coexist.

Furthermore, the concepts of the compressible and incompressible flow represent two fundamental classifications that describe how fluids behave under the different conditions. The compressible flow occurs when the fluid density changes significantly in response to the variations in the pressure and temperature. This behavior is typically observed in the gases, where the density and volume are highly sensitive to the external forces. The compressible flow typically occurs for the gases at the high speeds with the Mach number exceeding 0.3 [126]. The incompressible flow assumes that the fluid density remains constant during the motion, even under the pressure and temperature changes. This assumption is generally valid for the liquids, which are much less compressible than the gases. In addition, the incompressible flow is usually assumed for the gases at the low speed with the Mach number less than 0.1 [127]. The assumption of the incompressible flow makes the calculation time lower, since the density is not a variable, however, such simplification can negatively impact the simulation results, therefore, this aspect should be taken into account.

The Mach number is a dimensionless quantity that represents the ratio of the speed of an object - u to the speed of sound - c in the surrounding medium. The Mach number (Ma) is calculated by Equation (2-38):

2. Theoretical background

$$Ma = \frac{u}{c} \quad (2-38)$$

The speed of sound - c depends on the properties of the medium, particularly its temperature and pressure [128]. For an ideal gas, the speed of sound is given by:

$$c = \sqrt{k R_{spec} T} \quad (2-39)$$

where R_{spec} - specific gas constant is the gas constant divided by the molar mass of the gas, T is the temperature. k is the heat capacity ratio:

$$k = \frac{c_p}{c_v} = \frac{F+2}{F} \quad (2-40)$$

Therefore, the maximum speed of gas which will result in $Ma < 0.3$ is calculated for argon, air and methane, the gases which are relevant for the plasma reactors. Figure 2-14 shows the speed limits at different temperatures, giving the limits under which the flow could be considered incompressible.

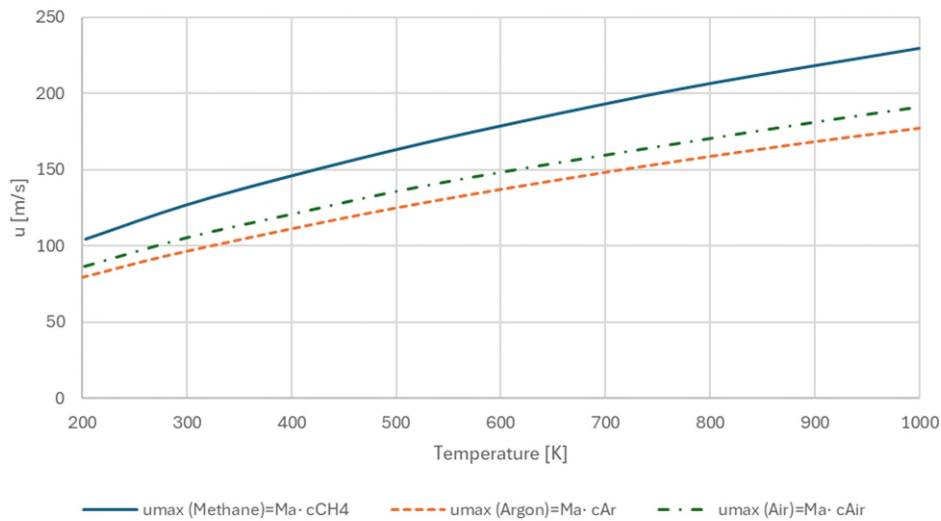


Figure 2-14 Maximum speed of Ar, air and CH₄ to consider incompressible flow.

From the results shown in Figure 2-14, it can be deduced that velocities up to 100 m/s and at room temperature can be approximately treated as incompressible for all gases treated. It is also evident that the speed at which the gases can be regarded as incompressible is proportional to the temperature. However, for very high temperature gradients, the gas density changes become too apparent, therefore, the type of the flow simulation (compressible or incompressible) has to be considered carefully. As soon as a large temperature difference occurs, the simulation should be calculated with the compressible flow. This is the case when a plasma arc with the local gas temperatures of several thousand Kelvin moves through the gas at the ambient temperature. In addition to the density, other gas properties, for instance,

the viscosity, change with the temperature. Therefore, the temperature dependent properties should not be omitted during the simulation.

2.5.3 Turbulence models

In theory, all continuous flows can be described with the Navier-Stokes equation, including the turbulent flows. In the computational fluid dynamics, the numerical solution of Navier-Stokes equation without any turbulence model is referred to as the direct numerical simulation, often abbreviated to DNS. If DNS is employed, the computational mesh and thus, the time steps must be selected very finely. This is highly computationally demanding and is not widely used on an industrial scale. Main application of DNS is to research the turbulence for simple geometries, as the computational effort is currently too high even for the super computers to deliver the results in reasonable times [129]. Recently, the artificial intelligence have been widely used for the turbulent flow simulations, but the models are still under the development [130]. In most cases, the exact resolution of the turbulent flow is not of interest, but rather its effect on the heat and mass transport.

The alternative method to DNS regarding the solution of the Navier-Stokes equations is the use of the turbulence models. In this work the turbulence models that are based on “Reynolds-averaged Navier-Stokes equations” (RANS) are considered. These are models that are associated with the comparatively low computational effort and are widely used in industry. There are other models, such as the “large-eddy simulation” or “detached-eddy simulation”, which are, however, significantly more complex and time consuming to simulate [131]. Therefore, they were not applied in the simulation.

The RANS equations are derived from the general Navier–Stokes equations using a method called the Reynolds decomposition, which divides the instantaneous flow quantities into their time-averaged and fluctuating components. This approach allows for the examination of the complex turbulent flows by focusing on their time-averaged behavior, while also accounting for the turbulence effects through the additional modeling terms. For instance, the instantaneous flow variables are separated into the mean and fluctuating components [132]:

$$u = \bar{u} + u' \quad (2-41)$$

$$p = \bar{p} + p' \quad (2-42)$$

here $\bar{u}$ and $\bar{p}$ are the time-averaged mean velocity and pressure, whereas u' and p' are the fluctuating components.

Substituting Equations (2-41) and (2-42) into the Navier-Stokes equation, and applying a the time-averaging operation, the governing equations are transformed into a set of the equations that describe the mean flow field:

2. Theoretical background

$$\nabla \cdot \bar{\mathbf{u}} = 0 \quad (2-43)$$

$$\frac{\partial \bar{\mathbf{u}}}{\partial t} + (\bar{\mathbf{u}} \cdot \nabla) \bar{\mathbf{u}} = -\frac{1}{\rho} \nabla \bar{p} + \nu \nabla^2 \bar{\mathbf{u}} + \bar{\mathbf{f}} - \nabla \cdot \overline{\mathbf{u}' \otimes \mathbf{u}'} \quad (2-44)$$

The last term $\overline{\mathbf{u}' \otimes \mathbf{u}'}$ is the Reynolds stress tensor (τ^{Re}) that represents a portion of the total stress tensor within the fluid that arises from averaging the operations applied to the Navier-Stokes equations, addressing the turbulent variations in the momentum. The Reynolds stress tensor is calculated by:

$$\tau_{ij}^{Re} = \rho \nu_t \left(\frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial \bar{u}_j}{\partial x_i} \right) - \frac{2}{3} \rho k \delta_{ij} \quad (2-45)$$

$$\delta_{ij} = \begin{cases} 1, \forall i = j \\ 0, \forall i \neq j \end{cases}$$

τ_{ij}^{Re} is found from the applied turbulence models.

The energy equation becomes:

$$\frac{\partial \bar{\rho} \bar{\varepsilon}}{\partial t} = \nabla \cdot \left(\bar{\rho} \bar{\varepsilon} \bar{\mathbf{u}} + \bar{\mathbf{u}} \bar{p} + \frac{2}{3} \bar{\rho} k \bar{\mathbf{u}} + q_{eff} \right) \quad (2-46)$$

$$q_{eff} = \alpha_{eff} \nabla \varepsilon \quad (2-47)$$

where q_{eff} is the turbulent heat flow and α_{eff} is the effective thermal diffusivity derived from the turbulent Prandtl number (Pr_t):

$$\alpha_{eff} = \frac{\rho \nu}{Pr} + \frac{\rho \nu_t}{Pr_t} \quad (2-48)$$

The turbulent Prandtl number is set to $Pr_t = 0.85$, which is an empirical value [133].

To adequately capture the effects of the turbulence when using a coarser computational grid and the larger time steps, it is essential to incorporate turbulence modeling. The commonly utilized models include the k- ε model, k- ω model, Shear Stress Transport (SST) model and Reynolds Stress Model (RSM) [134] [135] [136].

The k- ε model is perhaps the most widely utilized RANS turbulence model that employs two transport equations: one for the kinetic energy (k) and one for its dissipation rate (ε). The k- ε model is known for its robustness and reasonable accuracy in a wide range of the applications, including the wall-bounded flows. The k- ε model is typically used as the “high Reynolds number turbulence model” [134]. k- ω model differs in that it solves an equation for the specific rate of dissipation (ω) instead of ε . The k- ω model is particularly effective in simulating the flows with the strong adverse pressure gradients and those that are more sensitive to the flow separation. The k- ω model is usually applied for “low Reynolds number

turbulence modeling” [135]. There is a hybrid between both k- ϵ and k- ω , such as the k- ω -SST-Model, where near the wall regions are calculated by the k- ω model, since the velocity near the wall is lower and, hence, the Reynolds number is lower. Consequently, the k- ϵ model is applied for the rest of the domain [136]. RSM goes beyond the eddy viscosity models by providing a complete treatment of the Reynolds stresses. It solves the additional transport equations for each stress component, thereby capturing the complex anisotropic turbulence effects. RSM is often employed in the situations where the flow anisotropy is significant or where the standard models fail to provide the accurate predictions [134].

In this work k- ω -SST-Model is applied in some cases, due to its ability to capture the near-wall and far-field turbulence effects, and handle the adverse pressure gradients, while still being robust.

For both the low Reynolds and high Reynolds models, certain requirements for the design of the computational mesh are necessary. Two dimensionless parameters are used to describe the flow close to the wall. The dimensionless wall distance y^+ and the dimensionless velocity u^+ . y^+ and u^+ are defined in Equations (2-49) and (2-50):

$$y^+ = \frac{\rho y_{\perp} u_{\tau}}{\mu} \quad (2-49)$$

$$u^+ = \frac{u}{u_{\tau}} \quad (2-50)$$

where $y_{\perp}$ is the distance normal to the wall, u_{τ} is the friction velocity found through the wall shear stress τ_w in Equation (2-51):

$$u_{\tau} = \sqrt{\frac{\tau_w}{\rho}} \quad (2-51)$$

Depending on the region where either the k- ϵ or k- ω models are applied, different wall functions need to be calculated accordingly. The wall functions help to compute near the wall region more accurately, by connecting the viscous sublayer near the wall and the fully developed turbulent region. This approach reduces the mesh size, otherwise, if high Reynolds turbulence model, such as, k- ϵ is applied to a very thin boundary layer, the grid must be fine to resolve the calculation.

Figure 2-15 below contains the visual representation of the different layers at the wall. It also visualizes the correlation between the dimensionless wall distance y^+ and the dimensionless velocity u^+ .

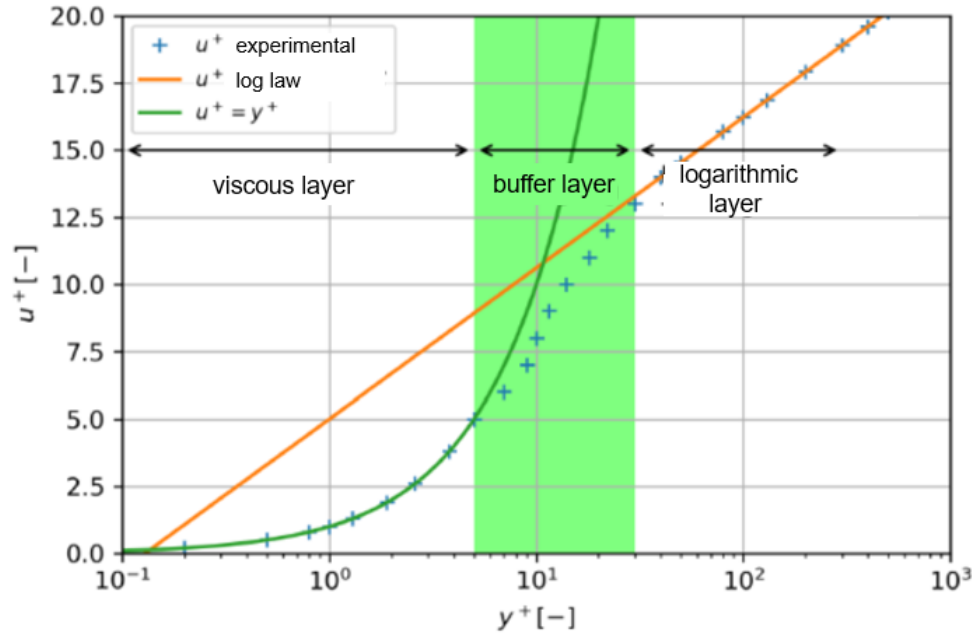


Figure 2-15 Wall function regions [137].

As shown in Figure 2-15, there are 3 main areas near the wall:

- The viscous layer for $y^+ < 5$. In this region the viscous effect prevails and following the assumption known as the “linear velocity law” is valid:

$$u^+ = y^+ \quad (2-52)$$

- The buffer layer for $5 < y^+ < 30$. It is the transition area from the viscous layer to the turbulent area. Here both the viscous and turbulent effects have similar impact.
- The logarithmic layer for $y^+ > 30$. The turbulence is fully developed in this region, and the velocity profile can be described by the logarithmic function:

$$u^+ = \frac{1}{k_K} \ln(y^+) + B_K \quad (2-53)$$

where the Karman constants are $k_K = 0.41$ and $B_K = 5.2$.

2.5.4 k- ω -SST-Model

The k- ω SST model operates by solving two transport equations: one for the turbulent kinetic energy (k) and another for the specific dissipation rate (ω). The formulation is designed such that it utilizes the k- ω model in the near-wall region, where the precise boundary layer behavior is essential, while switching to a k- ϵ model-like formulation in the free-stream region to maintain the sensitivity to the turbulent fluctuations away from the boundaries [138]. The governing equations for the k and ω terms can be expressed as follows [139]:

$$\frac{\partial(\rho k)}{\partial t} + \nabla \cdot (\mathbf{u} \rho k) = P_k - \beta^* \rho \omega k + \nabla \cdot [(\mu + \sigma_k \mu_t) \nabla k] \quad (2-54)$$

$$\frac{\partial(\rho \omega)}{\partial t} + \rho \mathbf{u} \cdot \nabla \omega = \frac{\gamma}{\nu_t} P_k - \beta \rho \omega^2 + \nabla \cdot [(\mu + \sigma_\omega \mu_t) \nabla \omega] + 2(1 - F_1) \rho \sigma_{\omega 2} \frac{1}{\omega} \nabla \omega \cdot \nabla k \quad (2-55)$$

where the turbulent viscosity μ_t is calculated by (2-56) and the production term of the turbulence kinetic energy P_k is determined by (2-57):

$$\mu_t = \frac{\rho a_1 k}{\max(a_1 \omega; b_1 F_2)} \quad (2-56)$$

$$P_k = \mu_t \left(\nabla \mathbf{u} : (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} (\nabla \cdot \mathbf{u})^2 \right) - \frac{2}{3} \rho k \nabla \cdot \mathbf{u} \quad (2-57)$$

The blending functions F_1 and F_2 and cross-diffusion term $CD_{k\omega}$ are calculated by:

$$F_1 = \tanh \left\{ \left\{ \min \left[\max \left(\frac{\sqrt{k}}{\beta^* \omega y}, \frac{500 \mu}{\rho y^2 \omega} \right), \frac{4 \sigma_{\omega 2} k}{CD_{k\omega} y^2} \right] \right\}^4 \right\} \quad (2-58)$$

$$F_2 = \tanh \left[\left[\max \left(\frac{2 \sqrt{k}}{\beta^* \omega y}, \frac{500 \mu}{\rho y^2 \omega} \right) \right]^2 \right] \quad (2-59)$$

$$CD_{k\omega} = \max \left(2 \rho \sigma_{\omega 2} \frac{1}{\omega} \nabla \omega \cdot \nabla k, 10^{-10} \right) \quad (2-60)$$

y is the distance to the wall, and the model constants are: $\beta_1=0.075$, $\beta_2=0.0828$, $\gamma_1=5/9$, $\gamma_2=0.44$, $\sigma_{k1}=0.85$, $\sigma_{k2}=1$, $\sigma_{\omega 1}=0.5$, $\sigma_{\omega 2}=0.856$, $\beta^*=0.09$, $a_1=0.31$, $b_1=0.31$ [139].

With the k - ω SST model an automatic wall treatment can be employed, where the results are independent on the mesh size. The blending approach allows for the solution of ω for the viscous and logarithmic layer:

$$\omega = \sqrt{\omega_{vis}^2 + \omega_{log}^2} \quad (2-61)$$

$$\omega_{vis} = \frac{6\rho}{\mu \beta_1 y^2} \quad (2-62)$$

$$\omega_{log} = \frac{\sqrt{k}}{C_\mu k y} \quad (2-63)$$

where $C_\mu = 0.09$.

As for the boundary conditions, the following conditions apply at the normal to the boundary (n):

$$\frac{\partial k}{\partial n} = 0; \quad \frac{\partial \omega}{\partial n} = 0; \quad \frac{\partial \bar{u}}{\partial n} = 0 \quad (2-64)$$

2. Theoretical background

Additionally, the wall is subject to the no-slip boundary condition:

$$\overline{u_{wall}} = 0 \quad (2-65)$$

A fully developed flow is assumed at the reactor inlet, while the following boundary conditions are imposed at the outlet:

$$p = 1 \text{ atm} \quad (2-66)$$

$$\nabla k|_{out} = 0 \quad (2-67)$$

$$\nabla \varepsilon / \nabla \omega|_{out} = 0 \quad (2-68)$$

2.5.5 Meshing techniques

One of the critical steps in the computational fluid dynamics is discretizing the reactor geometry into the appropriate elements, where the governing equations are to be solved. The mesh can influence the simulation accuracy, convergence and computations efficiency. The high-quality meshes significantly improve the accuracy of simulation results. A finer mesh provides a more detailed representation of the flow features, such as the boundary layers, turbulence structures, and other critical physical phenomena [140]. Proper meshing is crucial to achieving the numerical convergence. A mesh that is too coarse may lead to the significant numerical errors, while an excessively refined mesh can increase the computational cost without the substantial gains in the accuracy. Achieving the mesh independence, where the results no longer significantly change with the further mesh refinement, is essential for the reliability of the simulation results [141].

There are several types of meshes. The meshes can be generally categorized into the structured, unstructured and hybrid mesh. The structured mesh, as the name suggests, creates the grid-like pattern, which is suitable for the regular geometries [142]. The examples of the structured mesh types are the hexahedral and quadrilateral meshes, which offer a better numerical stability, convergence, and computational efficiency due to their consistent topology [143]. Also, the structured mesh provides a high accuracy, because it minimizes the truncation error and enhances the iterative convergence rate compared to the unstructured alternatives [143]. However, it is difficult to create a structured mesh for the complex geometries. The unstructured mesh oppositely does not have a regular pattern, and contains the triangle, tetrahedral and polyhedral shapes. The unstructured mesh permits the localized refinement around the areas of interest, which enhances the resolution without a proportionate increase in the mesh count, leading to a more time-efficient simulation [144]. Though, due to an irregularity in the cell arrangement, the unstructured mesh can create a larger numerical error and lead to the less accurate simulation results [143].

The combination of the structured and unstructured mesh is called a hybrid mesh. The hybrid mesh can quickly adapt to the complex geometries without incurring the excessive computational costs. In the realm of turbulence modeling, hybrid meshes can improve the prediction accuracy. For example, the structured grid can be applied to the near-wall regions, for a better boundary layer resolution, while the unstructured mesh can represent a turbulent region, due to the flexibility in its arrangement [145].

Many of the CFD simulation tools offer an automated mesh generation. The creation of a good mesh manually requires the skills and knowledge. Also, the automated meshing algorithms can adapt the mesh resolution based on the physical characteristics, ensuring that the critical regions such as the boundary layer or the regions with the high gradients possess sufficient refinement while minimizing the total number of elements. Figure 2-16 visually demonstrates the step-by-step meshing procedure for the GAP reactor using the mesh generation tool snappyHexMesh, incorporated within the OpenFOAM® software [146]. This meshing tool generates the unstructured mesh, mainly containing the hexahedral cells. As presented in Figure 2-16, initially the 3D geometry of the reactor was defined. Then a coarse mesh was created over the whole computational domain, including the background. Then the mesh was refined at the surface, where the boundary layer was located. Afterwards, the background was removed, followed by the “snapping” step, to align the mesh to the geometry of the reactor. Finally, more mesh refinement was added.

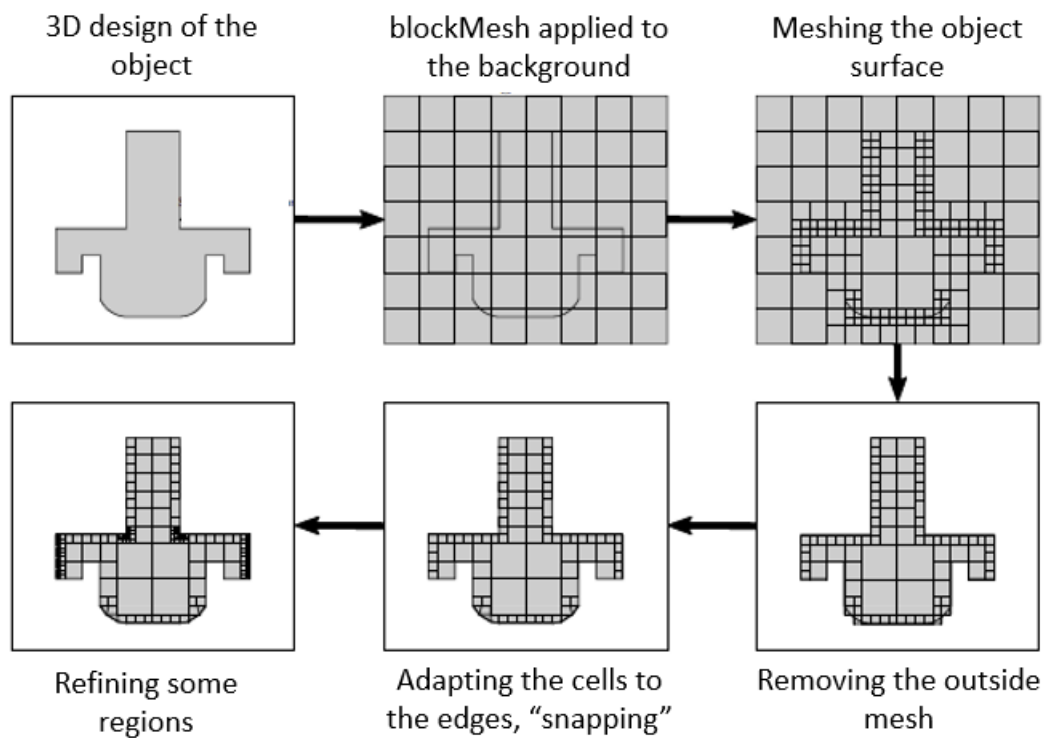


Figure 2-16 Meshing procedure example with snappyHexMesh in OpenFOAM®.

2. Theoretical background

The geometry of the GAP reactor is mainly cylindrical, where the cathode cap, the gas outlet with the inlets are circular in the cross-section. Whereas the cells built by snappyHexMesh are hexahedral. The mesh is refined at the boundary layer shown in Figure 2-17. However, the close-up of the central regions of the reactor displays some irregularity in the mesh pattern. This is the feature of auto-generated mesh, where the tetrahedral shapes of different sizes are used to fill the gaps.

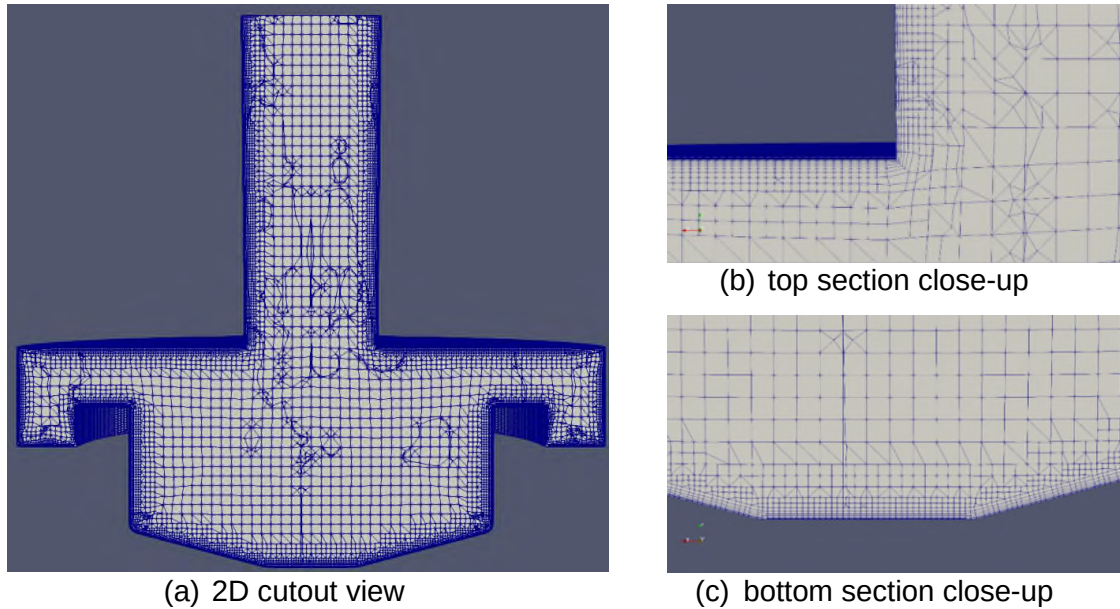


Figure 2-17 2D cutout view of the GAP reactor with hexahedral mesh and the boundary layer refinement.

Generally, to ensure that the created mesh does not affect the accuracy and the stability of the simulation, the mesh quality control is performed. Two critical aspects of the mesh quality are the non-orthogonality and skewness. The non-orthogonality refers to the angle between the adjacent mesh cell faces. In an ideal mesh, the faces of the adjacent cells should be orthogonal to each other. The non-orthogonal meshes can lead to the numerical errors in the solution [146]. Typically, the allowed degree of the non-orthogonality is 65° [146].

The skewness measures how much a mesh cell deviates from being a perfect shape, for instance, a cube for the hexahedral cells. It is defined as the ratio of the distance between the centroid of the cell and the centroid of the face to the length of the face [147]. Normally, the skewness of 4 is acceptable [146]. The mesh presented in Figure 2-17 has the orthogonality of 64.8 and the skewness of 3.7, consisting of over 900000 cells. A further mesh enhancement would require a higher number of cells, and as a result an increased simulation time, therefore, the given mesh quality was evaluated as satisfactory.

The GAP reactor was mainly represented by the hexagonal mesh. One of the reasons is that OpenFOAM® software was utilized to simulate the GAP reactor, which will be discussed later

in this work. As it was explained, OpenFOAM® is linked to the automatic meshing tool, which creates the hexahedral cells. On the other hand, the MW reactor domain was discretized into the tetrahedral cells. There, the Comsol Multiphysics® and Ansys Fluent® software were suited better to perform the simulations. The mesh generation tool in Comsol Multiphysics® and Ansys Fluent® prefers the tetrahedral cells [148] [149]. Thus, to aid the simulation convergence, the preferred software settings were selected.

Figure 2-18 contains the visual comparison between different meshes: hexahedral, polyhedral and tetrahedral. The arbitrary geometry was tested for the convergence, simulation time and the accuracy [150].

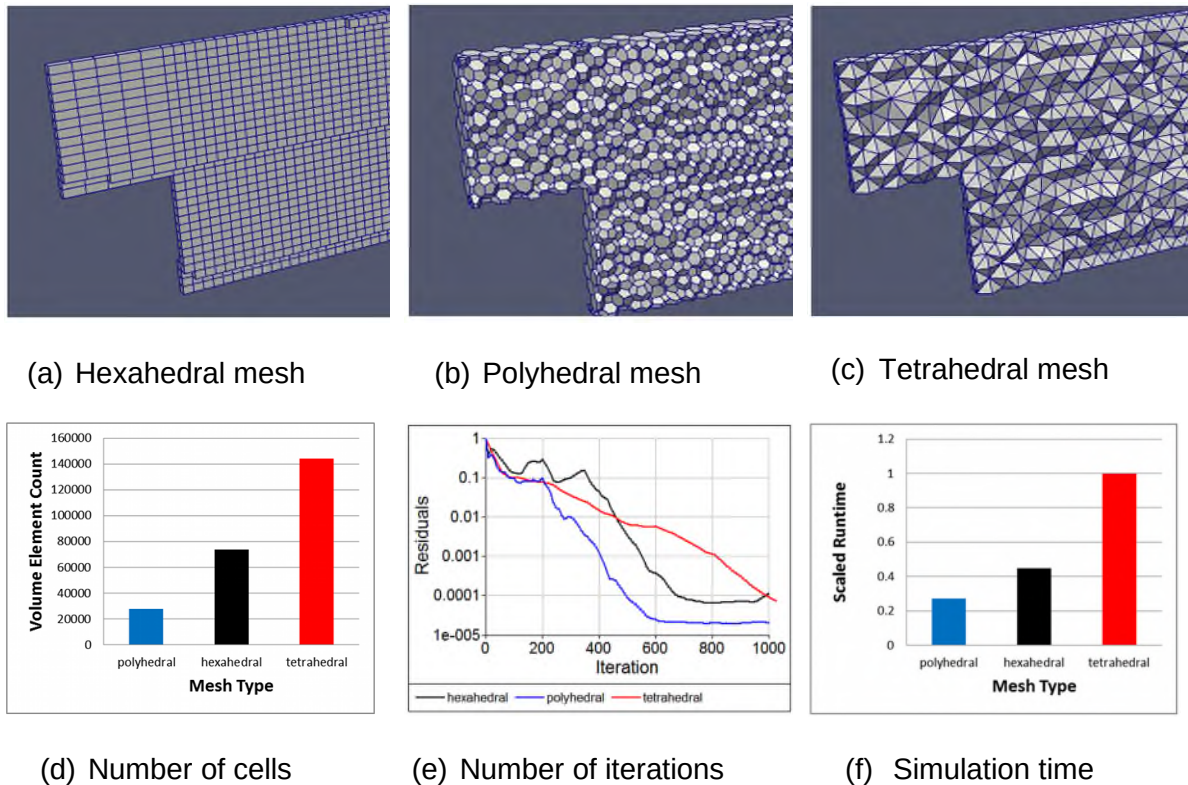


Figure 2-18 The comparison of various types of meshes, adapted from [150].

As shown in Figure 2-18, the polyhedral mesh required the fewest cells, which is expected since each polyhedron comprises multiple tetrahedrons. This led to the reduced simulation time. However, the polyhedral mesh is normally characterized by the high non-orthogonality and skewness, which can negatively affect the simulation accuracy. Additionally, its generation is more time-consuming and less straightforward compared to the hexahedral and tetrahedral meshes. The associated solution algorithms are also more complex [151]. Therefore, despite its advantages, the polyhedral mesh was not utilized in this study.

Generally, the sign of the good mesh is the low numerical error, fast convergence and small computational time. One of the most fundamental methods for the assessment of the mesh

2. Theoretical background

quality is conducting a mesh independence study. This involves performing simulations with multiple mesh densities to analyze the convergence of the results. By refining the mesh and observing the effects on the simulation outputs (such as velocity or pressure fields), the minimum mesh resolution required to achieve the consistent results can be identified [152]. This ensures an acceptable trade-off between the mesh quality and computational cost [153]. Since the mesh quality and number of cells are directly linked to the computational effort.

2.6 Fluid model of plasma

There are various methodologies employed in plasma modeling, which are classified broadly into the kinetic models, fluid models, and hybrid techniques, each with different advantages and disadvantages.

The kinetic models are designed to provide a detailed statistical description of the plasma particles, often utilizing the approaches such as the Particle-in-Cell (PIC) method or the direct simulation Monte Carlo (DSMC). The PIC method combines the Lagrangian particle simulation with the continuum electromagnetic field-solving methods, rendering it suitable for simulating both the low-temperature and high-temperature plasma. This method has been widely used to study the laser-plasma interactions and instabilities in the fusion plasmas, owing to its ability to model the intricate particle dynamics and electromagnetic effects realistically [154]. PIC can efficiently handle the complexities of the particle distribution functions under the varying electromagnetic field conditions, which enhances its application in the scenarios like the ion heating and electron acceleration [155]. However, this approach requires the vast computational resources and it is mathematically complex to apply.

The fluid models, on the other hand, compute the averaged properties of the plasma system using the macroscopic equations without resolving the motions of the individual charged particles. The magnetohydrodynamic equations are often the core of these simulations, enabling the simplified modeling of the large-scale plasma dynamics such as in the fusion reactors or industrial plasma processing systems [156]. The fluid models intrinsically assume a larger mesh perspective, thus, enabling the faster simulations compared to the kinetic approaches, which involve the detailed particle interactions. But such simplifications and assumptions may lead to some inaccuracies.

The hybrid models serve as an intermediary, incorporating elements of both the kinetic and fluid modeling techniques. For example, the hybrid plasma equipment model (HPEM) integrates a fluid model coupled with the Monte Carlo simulations to accurately describe the collisional phenomena in the plasma, particularly useful in the inductively coupled plasma systems [157]. This combination allows for more comprehensive analysis and enables to account for both the fluid dynamics and the microscopic particle interactions that are essential

for the accurate modeling of the plasma systems. On the other hand, the integration of different modeling techniques may be complicated and if incorrect parameters are selected, it can result in the wrong findings.

In this work, a fluid modeling approach was applied, due to the relative simplicity of the model. The fluid modeling portrays the macroscopic behavior of the fluid flow and magnetic field at the relatively low computational cost.

Here, the species in the plasma are observed as the components in the fluid, therefore, similar equations as in the previous sections could be applied for the plasma fluid flow [82]:

$$\frac{\partial n_k}{\partial t} + \nabla \cdot \Gamma_k + (\mathbf{u} \cdot \nabla) n_k = S_k \quad (2-69)$$

where n_k is the number density of the species k , Γ_k is the flux, S_k is the source term, $(\mathbf{u} \cdot \nabla) n_k$ is the term representing the species transport by the carrier gas.

The electron flux Γ_e and ion flux Γ_{ion} are found by the drift-diffusion approximation. And for the neutral species, Γ_0 , is it calculated by the Fick's law as follows:

$$\Gamma_{e,ion} = \pm \mu_{e,ion} n_{e,ion} E - D_{e,ion} \nabla n_{e,ion} \quad (2-70)$$

$$\Gamma_0 = D_0 \nabla n_0 \quad (2-71)$$

$\mu_{e,ion}$ is the mobility coefficient, $D_{e,ion}$ is the diffusion coefficient, E is the electric field. The positive or negative signs are defined by the direction of the drift velocity, "+" is used for the positively charged and "-" for the negatively charged species.

The transport parameters for the electron, μ_e and D_e , are obtained from the integration of the EEDF.

The mobility and drift diffusion coefficient for the neutral species and ions are calculated by:

$$\mu_k = \frac{\vec{e}}{m_k \nu_k} \quad (2-72)$$

$$D_k = \frac{k_B T_k}{m_k \nu_k} \quad (2-73)$$

where e is the electron charge, m_k is the mass, ν_k is the elastic collision frequency.

Similarly, the energy conservation equation is defined in terms of the average energy density $n_k \epsilon_k$:

$$\frac{\partial n_k \epsilon_k}{\partial t} + \nabla \cdot \Gamma_{\epsilon_k} \pm \vec{e} E \cdot \Gamma_k + \Theta_k = Q_{ext} - (\mathbf{u} \cdot \nabla) n_k \epsilon_k \quad (2-74)$$

$$\Gamma_{\epsilon_k} = -n_k \epsilon_k \mu_{\epsilon_k} E - D_{\epsilon_k} \nabla (n_k \epsilon_k) \quad (2-75)$$

2. Theoretical background

where Θ_k is the energy loss from elastic collisions, Γ_{ϵ_k} is the energy flux, $\vec{e} \cdot \Gamma_k$ is the energy flux due to the electric field E , Q_{ext} is the external energy source, μ_{ϵ_k} is the energy density mobility coefficient, D_{ϵ_k} is the energy density diffusion coefficient for the species k .

The electric field is calculated as the gradient of the electric potential:

$$E = -\nabla\varphi \quad (2-76)$$

and from the Poisson's equation:

$$\nabla^2\varphi = \frac{\rho_f}{\epsilon_{medium}} = \frac{\sum_k \pm \vec{e} \cdot n_k}{\epsilon_{medium}} \quad (2-77)$$

ρ_f is the charge density, ϵ_{medium} is the medium permittivity.

Another expression for the charge density and the electric potential is through the Debye length:

$$\frac{\rho_f}{\epsilon_{medium}} = \left(-\frac{1}{\lambda_d^2}\right)\varphi \quad (2-78)$$

The Debye length is the distance over which the plasma extends. It is specifically important for the non-thermal plasma, where the electrons and gas temperature are not in equilibrium. And it is calculated by:

$$\lambda_d = \sqrt{\left(\frac{\epsilon_{medium} k_B T_e}{n_e \vec{e}}\right)} \quad (2-79)$$

The boundary conditions are as follows:

$$\nabla T_{gas}|_{wall} = 0 \quad (2-80)$$

$$\nabla T_{gas}|_{outlet} = 0 \quad (2-81)$$

$$\nabla \Gamma_k|_{wall} = 0 \quad (2-82)$$

$$\nabla \Gamma_k|_{outlet} = 0 \quad (2-83)$$

2.6.1 0D plasma model

As discussed in the previous chapter, the number of the potential reactions occurring in the plasma can reach several thousand. Consequently, the reactions included in the 2D and 3D simulations must be carefully selected.

0D modeling can be utilized as the initial step to refine the reaction set in the plasma. 0D modeling helps to identify the non-essential reactions, hence, reduce the computational time in 2D and 3D. The 0D model observes only the temporal evolution of the reactions species [17]:

$$\frac{dn_i}{dt} = \sum_j (a_{ij}^{(2)} - a_{ij}^{(1)}) k_j \prod_l n_l^{a_{lj}^{(1)}} \quad (2-84)$$

where $a_{ij}^{(2)}$ and $a_{ij}^{(1)}$ are the stoichiometric coefficients of i -species on the left and right side of the reaction j , n_l is the number density of species on the left side of the reaction, k_j is the reaction rate given in (2-11) and (2-13).

After observing the formed reactive species, radicals and molecules, the reactions that have the most and least impact on the products achieved in the experiments can be identified.

2.7 Summary

This chapter provided a comprehensive overview of the plasma reactors used in the experiments: gliding arc plasma (GAP), microwave (MW) plasma, and surface dielectric barrier discharge (SDBD) plasma. It examined their fundamental characteristics, operational principles, and how they differ in behavior depending on the gas conditions such as temperature, pressure, and composition.

A detailed discussion was presented on the methane pyrolysis reactions within the GAP and MW plasma reactors. The chapter highlighted the unique nature of the plasma-induced reactions, contrasting them with conventional reactions that rely on the thermal activation. The plasma reactions, such as electron impact reactions, contribute to the non-thermal equilibrium between electron and gas temperatures, enabling the gas conversion at the substantially lower bulk gas temperatures, since the gas temperature is higher in the plasma region.

The fundamentals of plasma modeling, particularly as applied in the computational fluid dynamics (CFD) simulations, were also introduced. This included an explanation of the physical and chemical models used to represent the plasma, such as the energy transport, species generation, and the electromagnetic interactions.

Furthermore, the chapter explored different modeling dimensions: 0D, 2D, and 3D, used in the plasma simulations. Each approach was evaluated in terms of its complexity, computational cost, and accuracy. The zero-dimensional (0D) models offer simplicity and fast computation but lack the spatial resolution. The two-dimensional (2D) models provide a balance between the detail and computational efficiency, while the three-dimensional (3D) models deliver the most accurate spatial representation at the cost of the significantly higher computational resources.

The upcoming chapters will present the simulation results for the GAP, MW, and SDBD plasma reactors. These results will be compared with experimental data to validate the models and assess the opportunities that the simulation results opened.

3. GAP Reactor results and discussion

3.1 Introduction

This chapter presents the simulation results of the methane pyrolysis within the gliding arc plasma reactor. A bottom-up modeling approach was employed, beginning with the simplified representations using 0D and 2D models. These initial models helped to simplify the reaction mechanisms and the plasma behavior, providing the valuable insights that were used in the development of the more complex 3D model.

The 3D simulation was subsequently validated through the experimental testing, where the reactor geometry was modified based on the simulation outcomes. This optimization led to an increase in the methane conversion, demonstrating the effectiveness and practical relevance of the chosen modeling strategy.

3.2 Experimental setup

The gliding arc plasma reactor experiments were conducted in Ruhr-University Bochum, Chair of Applied Electrodynamics and Plasma Technology. The experimental setup shown in Figure 3-1 contains a direct current (DC) power supply with a maximum voltage and current 10 kV and 600 mA, a resistor of 15 k Ω and the gliding arc plasma reactor [88].

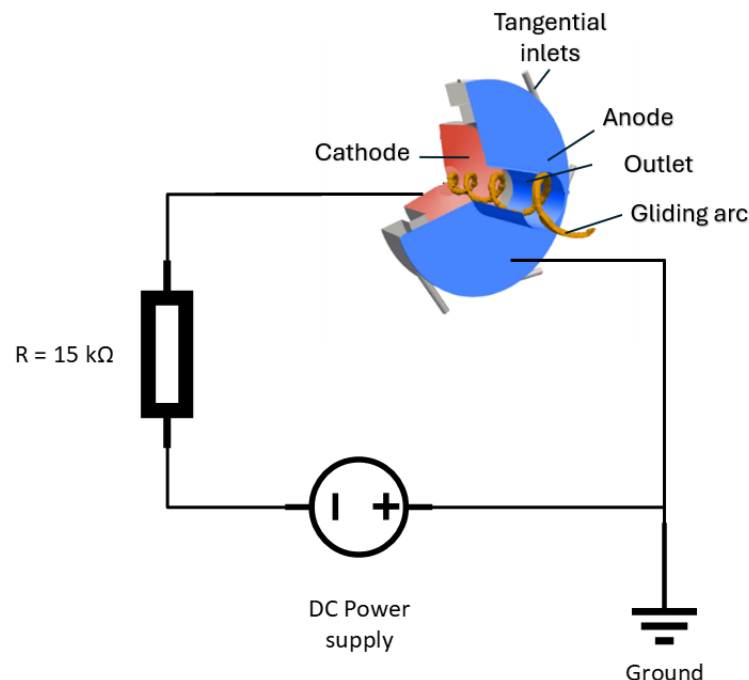


Figure 3-1 Experimental setup of gliding arc plasma.

The reactor consists of the cathode cap and anode outlet. There are 6 tangential inlets, where methane and the plasma carrier gas at 10 l/min of the total flow rate, are introduced inside the

reactor. In this case argon is the plasma carrier gas. The geometry of the inlet tubes allows the plasma arc to move throughout the reactor in the vortex flow, otherwise if the arc would stop in one place the electrical circuit would short-circuit from the accumulation of the local electric field. The vortex flow helps the arc to sustain itself for the entire time without extinguishing. Figure 3-2 shows the captured image of the arc protruding from the reactor outlet. The circular motion of the arc is noticeable in the front view of the outlet in Figure 3-2. Moreover, the circular gas motion exhibits a cooling effect on the reactor wall, thus, protecting the material. There is one outlet where the products and unconverted methane leave the reactor, which later can be separated in the downstream facilities.

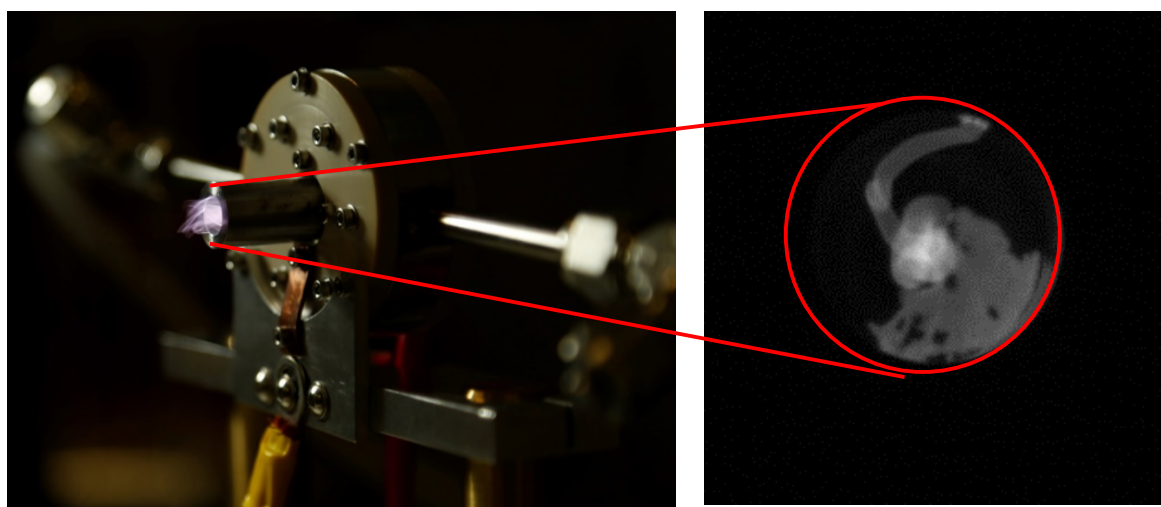


Figure 3-2 Gliding arc plasma photo: side and front view [158].

Over time different reactor geometries were experimentally investigated. The changes of the reactor geometries were based on the simulations made in this work. The suggested alterations improved the arc stability and methane conversion, which will be discussed in the later sections.

The original reactor geometry was based on the gliding arc plasma reactor for CO_2 conversion [55]. This design was first used to characterize the plasma parameters, such as the gas temperature inside plasma, the size of the plasma arc, the power settings needed to ignite the plasma [159]. Nitrogen was used for the initial characterization of the GAP reactor, since it is an easier molecule to initiate the arc in comparison to methane [159]. In subsequent experiments, methane was used as the reactant gas, while argon served as the plasma carrier gas. The GAP reactor used for the experiments with N_2 is pictured in Figure 3-3. The reactor had an original tangential inlet diameter of 1 mm, outlet diameter of 7 mm, and anode outlet tube length of 16 mm. The inlet diameter was later changed to 2 mm, due to more stable plasma arc, and the simulation results for the difference between 1 mm and 2 mm are presented here. The gap between the cathode cap and anode tube was 3 mm, and this was

3. GAP Reactor results and discussion

the narrowest distance between the electrodes, where the plasma was initiated. There is a region arbitrarily named “step”, which is depicted in Figure 3-3, where the inlet gas was circulated before entering the main reactor body.

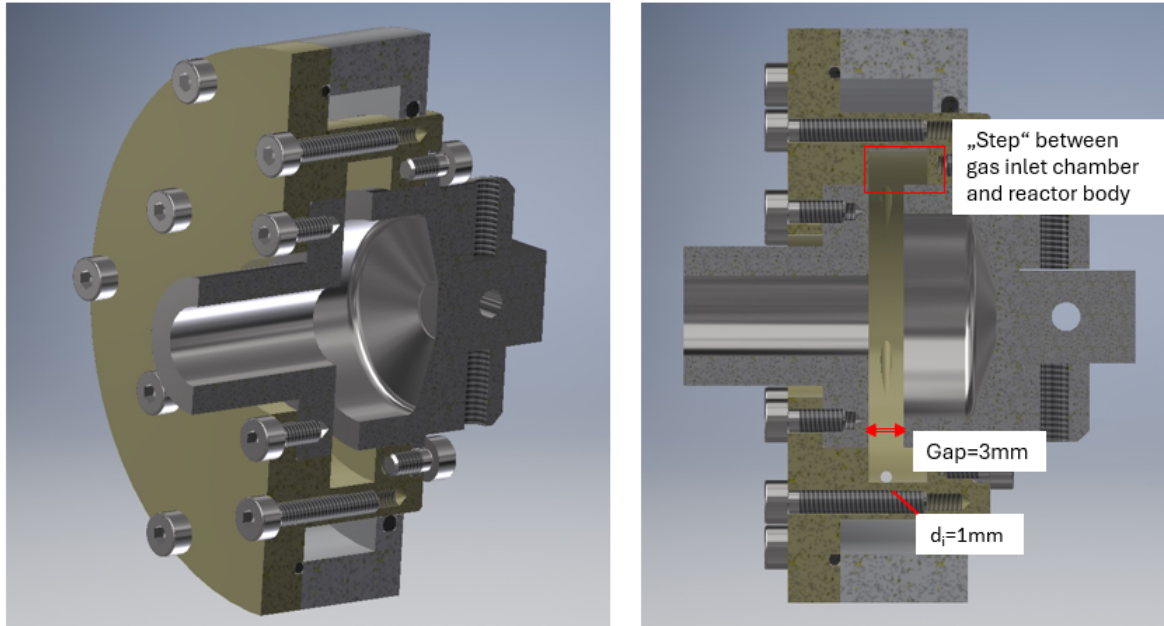


Figure 3-3 Original GAP geometry for N₂ gas [159].

The experiments showed the difficulty with the short-circuiting, the arc would not be ignited for longer time, hence, the methane conversion was limited. From a simulation perspective, the narrow geometry of this reactor section posed additional difficulties. Its confined shape and the presence of steep velocity gradients necessitated a highly refined mesh, increasing the computational cost. These combined experimental and modeling challenges prompted consideration of removing this part from the reactor design. The functionality of this “step” part of the reactor was evaluated in the further sections, therefore, in the later experiments, the reactor design excluded this “step” part [88].

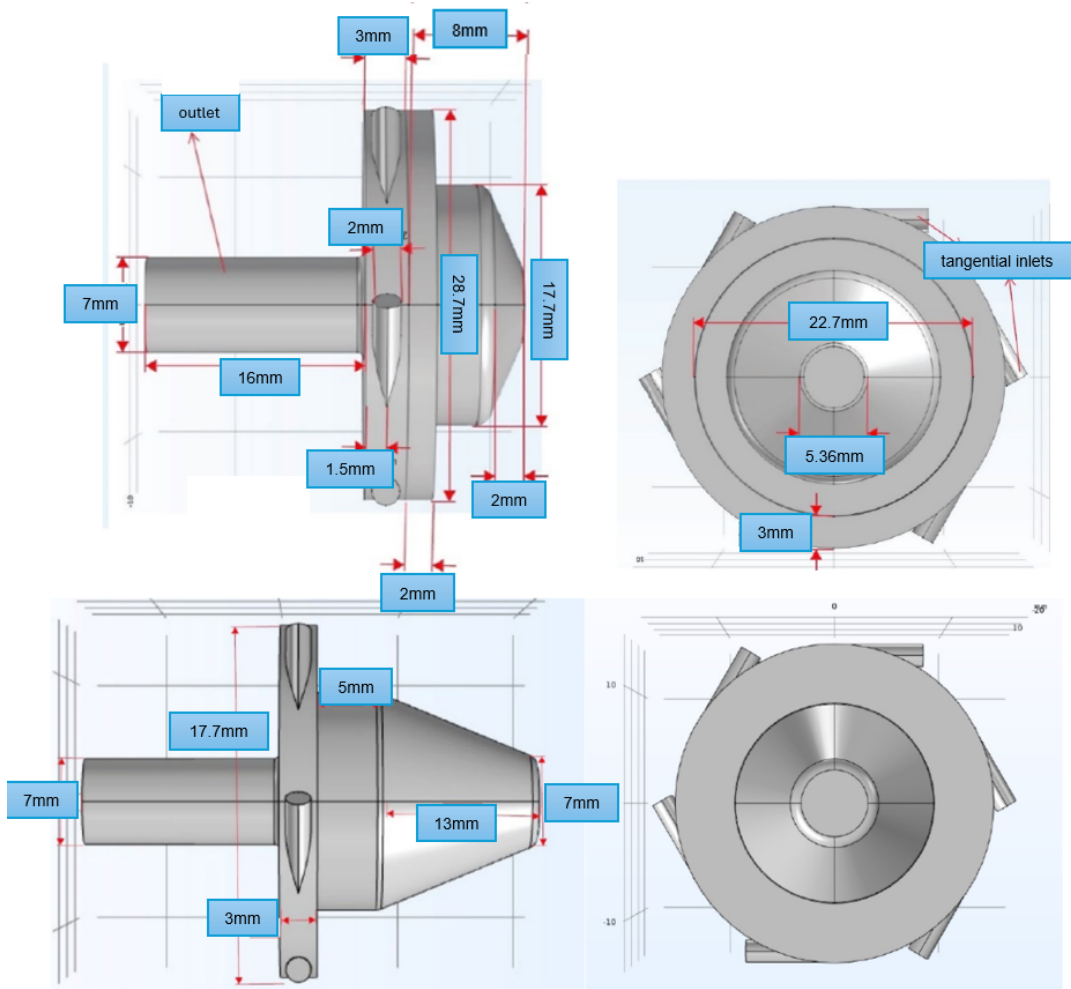


Figure 3-4 Reactor A (top) and B (bottom) for methane conversion [39] [88].

Two geometries, which were experimentally examined in [88] and [39] are shown in Figure 3-4. The maximum CH_4 conversion of 44 % was achieved for the Reactor B with 16 vol% CH_4 + 84 vol% Ar gas mixture [88]. Whereas for the unchanged reactor A, with the same feed gas composition, the CH_4 conversion of 35 % was observed [39]. This conversion improvement was achieved through the alterations in Reactor A geometry. For instance, the “step” was removed, which allowed for the flow to stabilize. Also, the cathode body was elongated from 8 mm to 13 mm, thus, the residence time in the reactor could be increased, allowing for the higher conversion of methane [88].

The sections later will give the results of the reaction set reduction, plasma arc simulation in 2D, and the 3D simulation results, where the arc acts as the heat source. Finally, the reactor design improvements will be summarized at the end.

3.3 0D simulation results

The complexity of the reaction set of methane pyrolysis in plasma was discussed in Section 2.4.1. In addition to pure methane pyrolysis, various carrier gases were simulated in the 0D model. Although during experiments Ar was used as the carrier gas, a 0D simulation with N₂ as the carrier gas was performed as well.

Initially, a simplified set of reactions including with electron impact reactions was simulated at $T_{\text{gas}} = 3000 \text{ K}$ to understand the main driving reactions in the gliding arc plasma [160] [48].

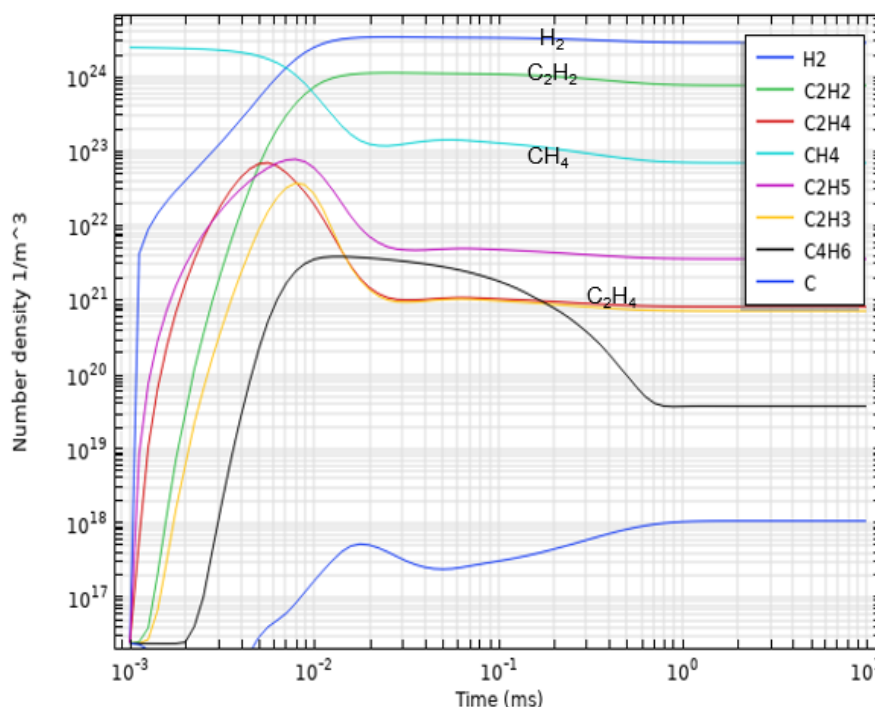


Figure 3-5 Number densities of products for CH₄ pyrolysis with simplified plasma.

Figure 3-5 shows the 0D modeling results involving the reaction set based on [160] enhanced with the electron impact reactions from [48]. The main produced species in the Figure 3-5 above are H₂ and C₂H₂. This is consistent with the experiments conducted in RUB, see Figure 3-6. In one of the experiments, 4 vol% CH₄ and Argon gas mixture was pyrolyzed in the GAP reactor with increasing applied current at 50 mA increment. Figure 3-6 exhibits that the gas analyzer detected ethyne (C₂H₂) and hydrogen (H₂), whereas the ethene (C₂H₄) was present in negligible amounts.

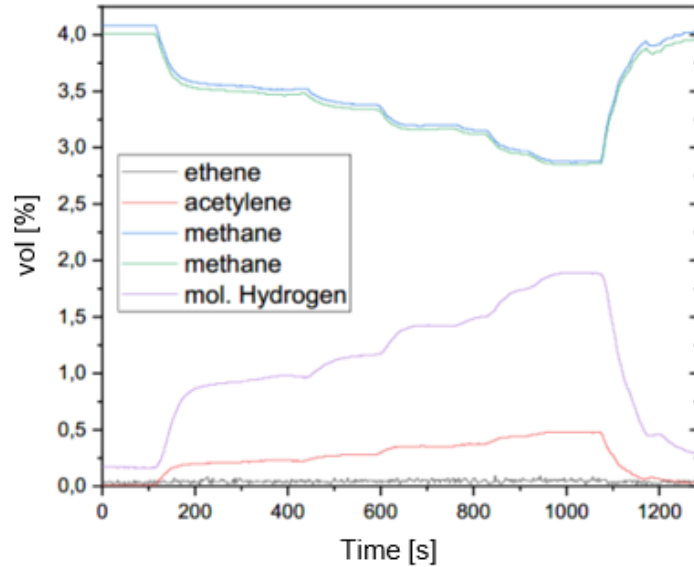


Figure 3-6 Gas analytics measurements with 4 vol% CH₄ at 10 l/min.

Schematically the reaction pathways can be depicted as in Figure 3-7. The width of the arrows represents the reaction rate. Figure 3-7 highlights the final products H₂ and C₂H₂.

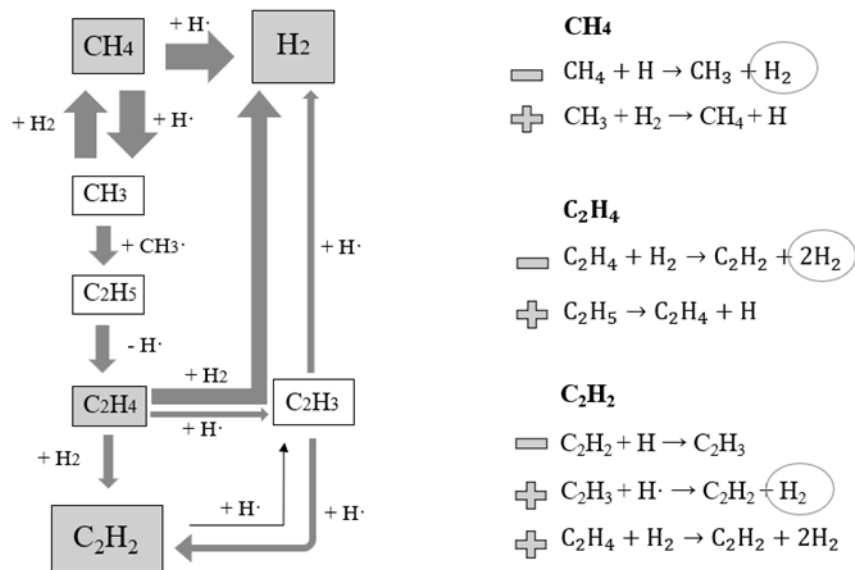


Figure 3-7 Main reaction pathways in GAP reactor [160]

Table 3-1 shows the CH₃ radical production reactions and their rates at 300 K and 3000 K. CH₃ radical is the initial species, which drives the conversion of methane further. The rates calculated at different temperature regimes demonstrate that inside the arc, where the gas temperatures can reach several thousand Kelvin, the temperature-dependent chemical reactions prevail. Whereas in the gas at ambient temperatures, but in the presence of the free electrons occurring from the arc, the electron impact reactions contribute to the formation of the reactive radical species.

3. GAP Reactor results and discussion

Table 3-1 CH₃ production rate mechanism at different temperatures.

Reaction	CH ₃ Production rate at 300 K [mol/(m ³ ·s)]	CH ₃ Production rate at 3000 K [mol/(m ³ ·s)]
CH ₄ + H → CH ₃ + H ₂	2.67E-06	1.5806
CH ₂ + H ₂ → CH ₃ + H	0.0004	0.0015
CH ₄ → CH ₃ + H	3.36E-66	0.0016
e + CH ₄ → CH ₃ + H + e	0.014	0.0019

Therefore, to achieve a representative reaction set, both thermal and electron impact reactions needed to be introduced in the model.

The reaction set used for the 0D simulation shown in Figure 3-5 included 43 reactions and 22 species [160], [48]. To evaluate the completeness of the previously applied simplified reaction set in Figure 3-5, another detailed reaction set was simulated in 0D.

Figure 3-8 shows the main products from a detailed plasma chemistry set with 34 species and 526 reactions [161], where H₂ was produced mainly, and only traces of C₂H₂ were illustrated. Note that CH₄ is not depicted, since it has a much higher n_e. Since only plasma chemistry related reactions are included, most CH₄ is unconverted at the given simulation time.

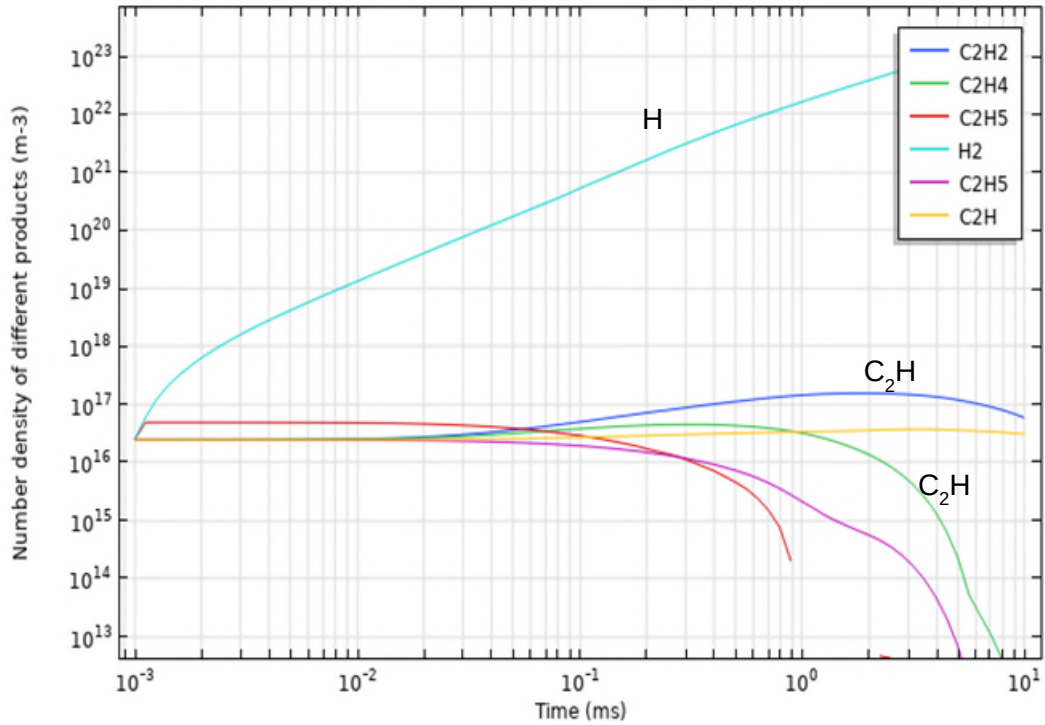


Figure 3-8 Number densities of products for CH₄ pyrolysis with detailed plasma reactions.

The simulation was performed at the atmospheric pressure, $T_{\text{gas}}=3000$ K and 10 l/min flow rate, with input power of 220 W.

The species included in the 0D simulation are listed in Table 3-2. The heavier species such as C₂H₆ and C₃⁺ hydrocarbons do not appear in Figure 3-8, due to their low number densities.

Table 3-2 The species included in the 0D simulation [161].

Neutral species	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 ₇ , C ₃ H ₆ , C ₃ H ₅ , C, C ₂ , H ₂ , H
Charged species	CH ₃ ⁺ , CH ₄ ⁺ , CH ₂ ⁺ , CH ⁺ , C ⁺ , C ₂ H ₆ ⁺ , C ₂ H ₅ ⁺ , C ₂ H ₄ ⁺ , C ₂ H ₃ ⁺ , C ₂ H ₂ ⁺ , C ₂ H ⁺ , C ₂ ⁺ , H ₃ ⁺ , H ₂ ⁺ , H ⁺ , H ⁻

The achieved simulation result in Figure 3-8 differs from the experimental results in Figure 3-6. Figure 3-8 proves that to simulate the GAP in the atmospheric pressure, it is not sufficient only to include the electron impact reactions and plasma reactions, even if more than 500 reactions are involved. The plasma reactions were, thus, enhanced by the thermal reactions from [160], and the results are presented in Figure 3-9.

3. GAP Reactor results and discussion

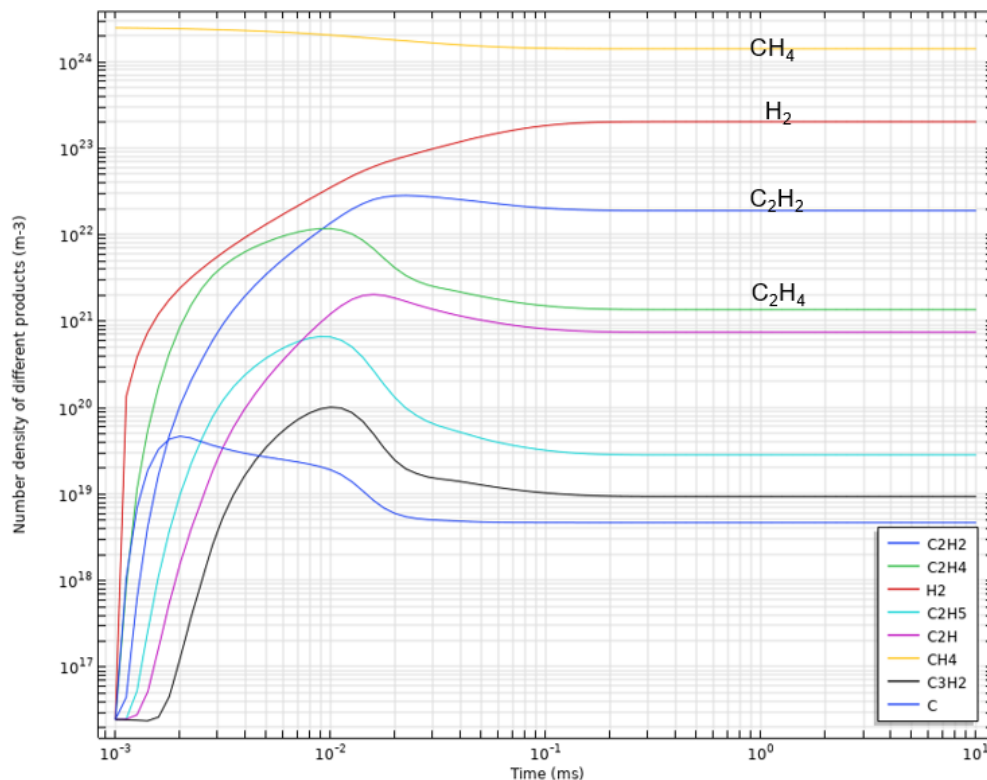


Figure 3-9 Number densities of products for CH₄ pyrolysis with detailed plasma reactions and thermal reactions combined.

In Figure 3-9 as in Figure 3-5 the main products are H₂ and C₂H₂, whereas the other species such as C₂H₄ are the intermediate ones. Since both results including ca. 500 reactions and ca. 40 reactions are similar, for further 2D and 3D simulations the simplified set of thermal and electron impact reactions, listed in Table 9-1, Table 9-2, Table 9-3 were utilized.

Also, the possibility of including the plasma carrier gases was simulated. For instance, Figure 3-10 shows the impact of different admixtures of Ar on the methane conversion.

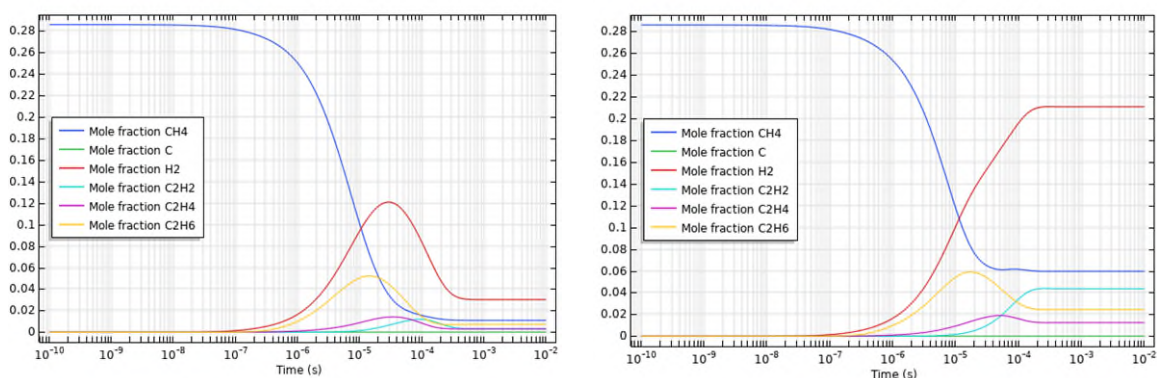


Figure 3-10 1:20 CH₄:Ar (left) and 6:15 CH₄:Ar (right) 0D simulation [17].

Comparing methane conversions in both diagrams in Figure 3-10, the mixture with more Argon shows almost full conversion. This is explainable, since Argon is an easier gas to ignite and sustain the plasma, due to its inert nature compared to methane. Therefore, when methane is diluted with the carrier gas, it is easier to convert since plasma is more stable. On the other hand, the hydrogen production on the left graph demonstrates a bell-shaped curve, because hydrogen is also consumed in some reactions. When the CH_4 concentration in the gas mix is higher, the reaction involving H_2 are less dominant. Therefore, more hydrogen can be produced, even at lower methane conversion. The reactions for CH_4 -Ar mixture are listed in Table 9-4.

One of the possible carrier gases is nitrogen. Before conducting the experiments, the production of poisonous HCN gas was simulated using the kinetics and reactions from the literature [92]. As shown in Figure 3-11, HCN is produced at high gas temperatures. Therefore, no CH_4 - N_2 mixture was used for the experiments with the plasma reactors, due to possible health risks. Pure nitrogen was used only for the plasma characterization [159].

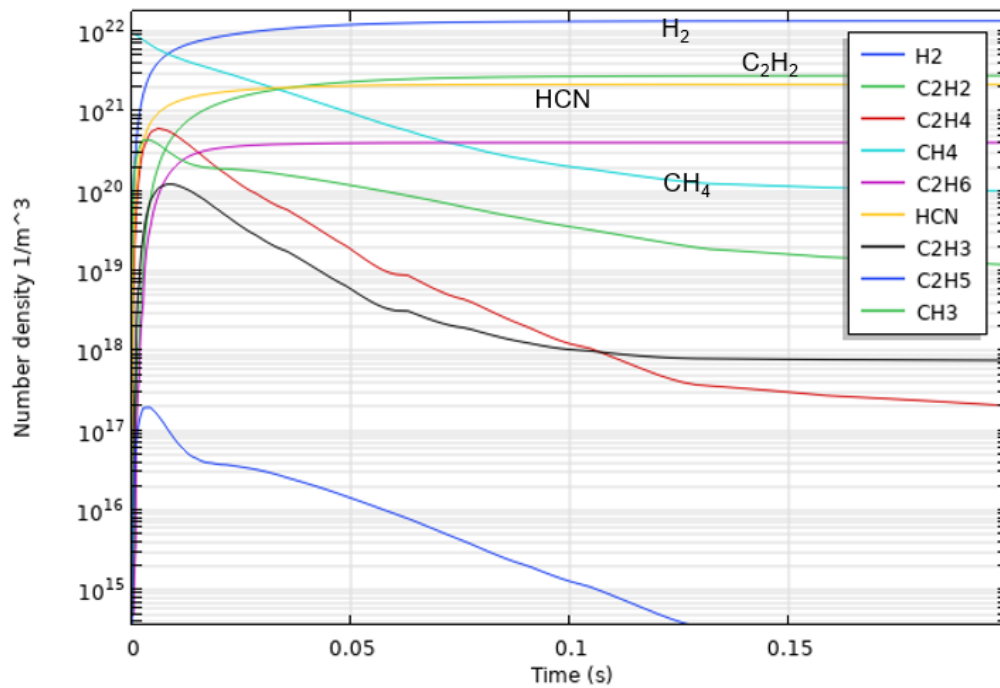


Figure 3-11 Calculated number densities for CH_4 - N_2 mixture with 1:5 ratio, at 2000 K.

The 0D simulation of different reaction sets helped to refine the reactions, and gain insight on the experimental setup optimization. The simplified reaction set was later used 3D simulations, which significantly lowers the computational time of 3D simulations. The outcomes are given in the subsequent sections.

3.4 Plasma simulation in 2D

Before combining the reactions set identified by 0D and the plasma modeling equations in 3D, a test in 2D was made first. This gave an estimation of complexity of plasma simulation in 3D, and gave an opportunity to simplify the simulation for less computational cost.

The simplified 2D geometry was simulated in the arbitrary geometry of 60 mm height and 44 mm width at the inlet and outlet. The gap between the electrodes was selected as 12 mm, which was based on the typical gliding arc length of the GAP reactor.

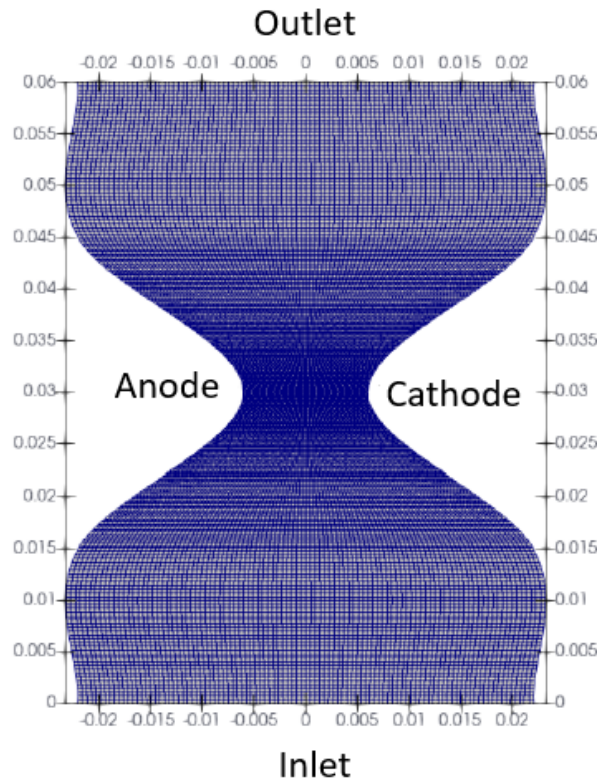


Figure 3-12 Mesh of the 2D gliding arc reactor.

The cell number in the Figure 3-12 is 20000. For comparison, the 3D model of the GAP reactor consisted of ca. 900000 cells. The number of cells is directly proportional to the computational time. Therefore, before applying the plasma equations and the large set of thermal and electron impact reactions to 3D reactor, first an attempt with 2D and the limited number of cells was done.

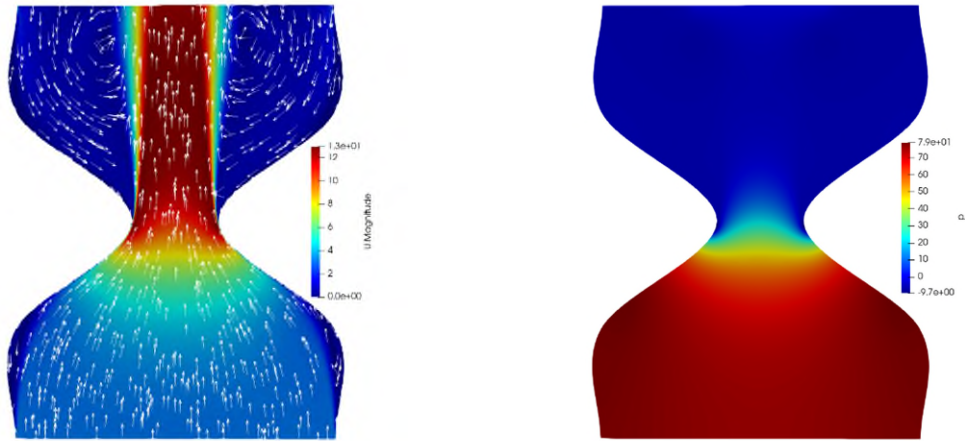


Figure 3-13 Velocity (m/s) (left) and pressure field (right) normalized over density ($\text{Pa}\cdot\text{m}^3/\text{kg}$) of the arbitrary geometry in 2D.

An arbitrary geometry in 2D, where the cathode and anode are on the opposite sides, and where the gas is flowing in the upwards direction between the electrodes, was simulated, as shown in Figure 3-13. The velocity magnitude was in the similar range as in 3D reactor, thus, the simulated arc movement due to the gas flow should be comparable. Moreover, the concave shape created the vortices towards the outlet of the 2D reactor, which imitated the eddies and turbulence in 3D. The simulation was done for $600\ \mu\text{s}$. After that the simulation broke down. Nevertheless, the obtained results explained the arc behavior and the insight was used in the 3D simulations.

Also, the complex methane pyrolysis chemistry was substituted by the Argon chemistry given in Table 2-3, in order to reduce the simulation time, and to allow the simulation to converge.

As it was explained in the previous sections, when the electrical current was applied to the gliding arc plasma, the arc ignited at the narrowest location between the electrodes.

Figure 3-14 shows the gas temperature at the arc initiation at $3 \times 10^{-6}\ \text{s}$, and the change in temperature after $6 \times 10^{-4}\ \text{s}$. Initially, when no arc was present, the whole domain was at the ambient temperature. And after the ignition of the arc and its propagation, the gas temperature around the arc rose to several thousand of Kelvin. This was due to the high electron temperatures in the arc. The gliding arc plasma is considered as the non-thermal plasma, because the gas normally stays at the ambient conditions, whereas only the arc is energized. Nevertheless, the arc itself exhibits high temperatures, therefore, the thermal reactions need to be considered [53].

3. GAP Reactor results and discussion

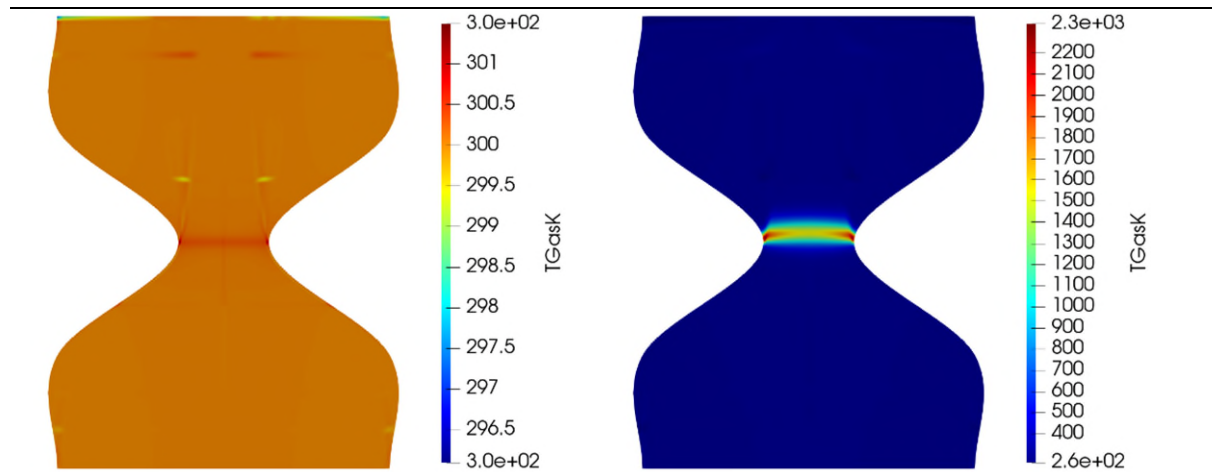


Figure 3-14 Gas temperature [K] for 3×10^{-6} s (left) versus 6×10^{-4} s (right).

Figure 3-15 pictures the gliding arc itself, at the ignition moment and after some time. Note that the Ar^+ ion number density is illustrated, which is equivalent to the electron density, since the ions and electrons were equally present. An interesting observation in Figure 3-15 is that the arc arched upwards, in the direction of flowing gas. In the gliding arc plasma experiments, the arc circulated in the reactor in the same direction as the gas. Therefore, this simulation demonstrated that the arc followed the gas flow.

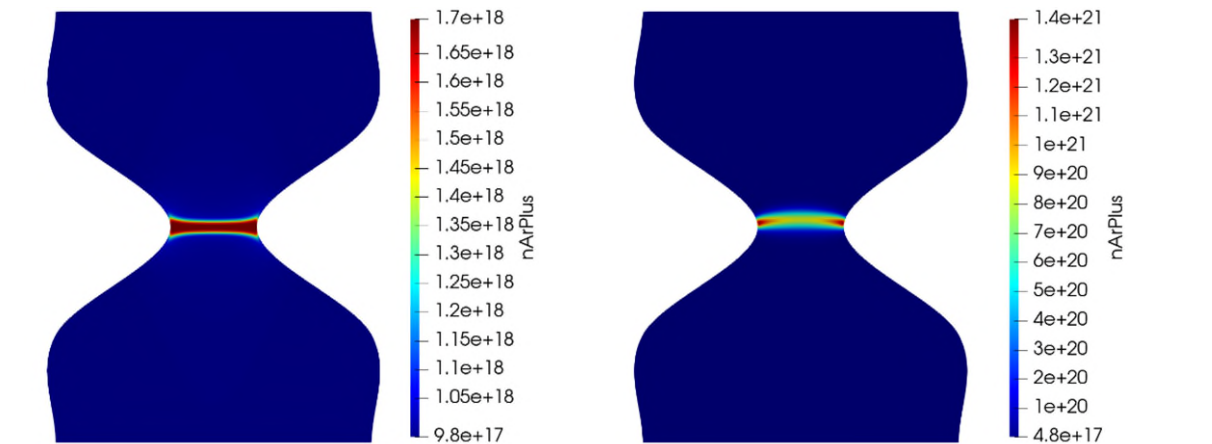


Figure 3-15 Number density of Ar^+ equivalently e^- [1/m^3] for 3×10^{-6} s (left) versus 6×10^{-4} s (right).

Moreover, the electron density magnitude was increased with time, which complies with the theory that with time the arc gains more energy. Therefore, it was vital to stabilize the arc for its continuity, in order to gain the electron density. The electrons then reacted with methane, and generated the reactive radicals and ions, which were converted to hydrogen, and other valuable products.

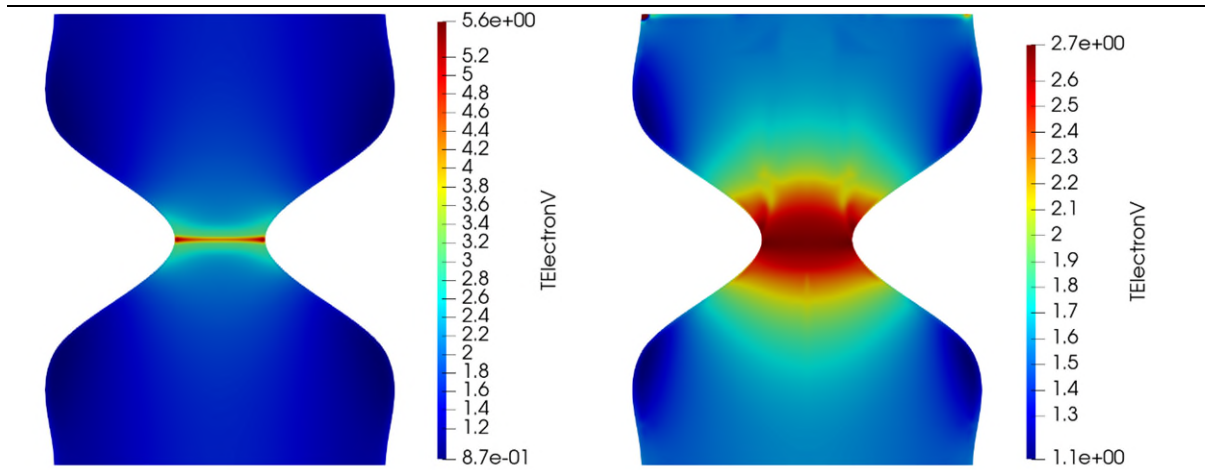


Figure 3-16 Electron temperature [eV] for 3×10^{-6} s (left) versus 6×10^{-4} s (right).

Figure 3-16 shows the electron temperature development with time. It is shown that with arc propagation, the electron temperature field was enlarged. This was due to the fact that electrons are low in mass and can be carried with the gas easily. Hence, the reaction location was not limited only to the arc, but also could happen in the vicinity.

As was mentioned before, the simulation stopped after 600 μ s. The applied simplifications such as the 2D geometry, which entails the gas flow only in the xy-direction, and Argon plasma chemistry instead of the complex methane pyrolysis could not balance out the computationally costly plasma equations. The convergence difficulty rose from too large gradients in the numerical simulation. The challenges of transitioning from 2D to 3D included: the magnitude range of the number densities $\sim 10^{20} \text{ m}^{-3}$, the temperature difference between the ambient gas and the arc is $\sim 10^3 \text{ K}$, and the arc diameter, which is $\sim 200 \text{ }\mu\text{m}$ [159], hence requiring fine mesh for the simulation. On top of it, the large set of reactions and their almost instantaneous reaction time in plasma made it almost impossible to converge the simulation with the turbulent vortex flow and plasma reactions in 3D.

Thus, the plasma was assumed as a heat source for the 3D simulation of GAP reactor, where the thermal reactions take place. As it was shown in the 0D simulation, at higher gas temperatures, the thermal reactions of methane conversion dominate. Also, in 2D plasma simulation the increase in the gas temperature in the arc was simulated. These results can be further joined, and the complete 3D simulations can be performed.

3.5 Simulation of GAP with plasma as the heat source

The complexity of the 2D plasma simulation was described in the previous section. To obtain a 3D simulation with the methane pyrolysis reactions, with the limited computational effort, the adjustment in the arc simulation needed to be made. In this section the results of the 3D

3. GAP Reactor results and discussion

simulations where the gliding arc was considered as the heat source are presented and discussed.

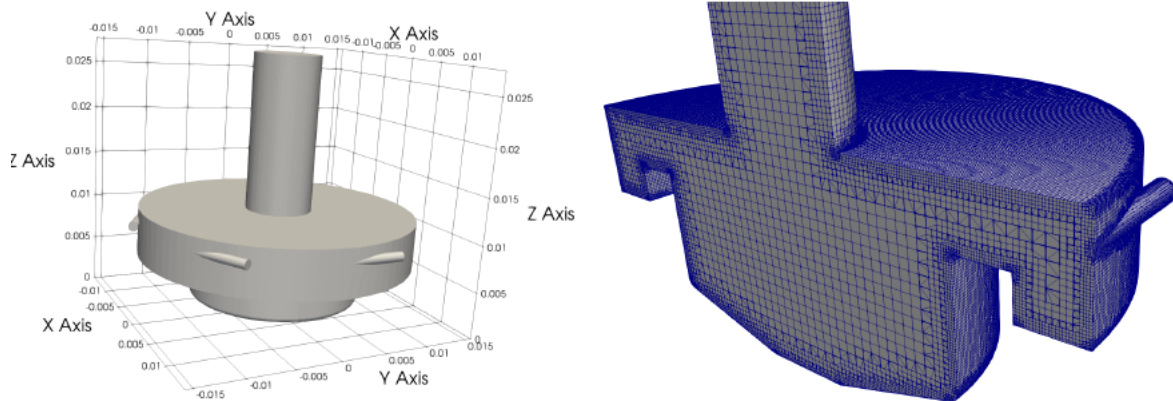


Figure 3-17 Mesh of the 3D GAP plasma reactor.

The mesh contained 902883 cells, 326204 were in the reactor body. The major number of the cells were contributed by the narrow inlet diameters. Moreover, the highest velocity, and respectively, the greatest turbulence occurred at the tangential inlets. Therefore, the mesh size was set to be fine enough to converge the simulation and reduce the computational error.

The photo of plasma Figure 3-2 indicated that the gliding arc rotated in the spiral motion following the gas. The arc diameter was approximately ca. 200 μm , which was seen at the anode spots in Figure 3-20, and the length was at the same range as the height of the reactor. Since the arc was not a straight line, a spiral shape was implemented as show in Figure 3-18.

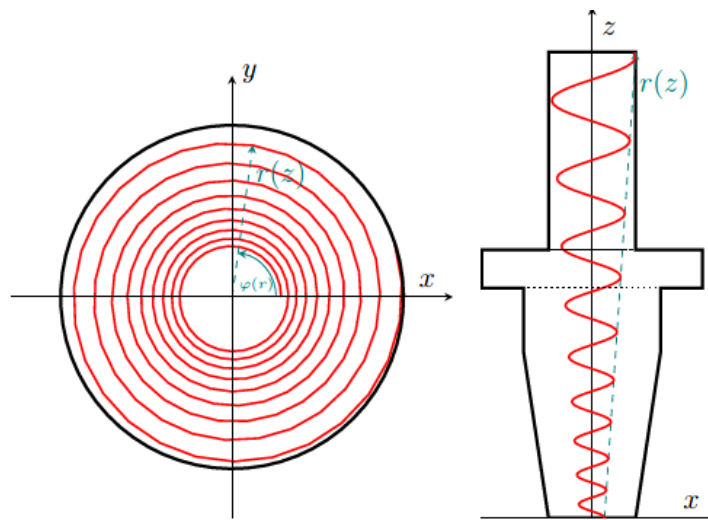


Figure 3-18 Gliding arc replacement with “artificial” arc.

The spiral rotated together with the gas, and was heated to 4000 K, which was equal to the average arc temperature measured in the experiments.

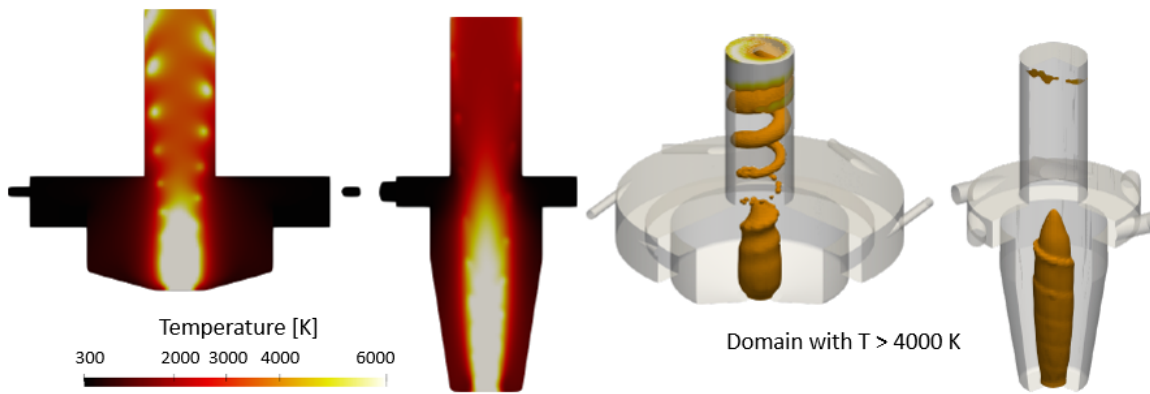


Figure 3-19 Temperature profile with the “artificial” arc for 2 geometries, without chemical reactions.

Figure 3-19 shows the temperature profile inside 2 different reactor geometries. These geometries will be discussed in the next section. The 3D simulations were carried out with the gas flow at 10 l/min and the arc temperature at 4000 K. The power supply during the experiments achieved maximum 10 kV voltage and maximum 600 mA current, therefore, the heat in the simulation was limited to 1000 W, to account for the efficiency and the heat losses. When both reactors Figure 3-19 are compared, both had the highest temperature at the arc. Even though the arc was extremely hot, the walls of the reactors were still at the ambient temperature, due to the vortex flow protecting the wall region from the heat. Also, as expected, the center of the vortex circulated the heat, hence, more thermal reactions could take place. Overall, the design with an elongated cathode cap demonstrated that relatively high volume of the gas in the reactor could be heated up in the arc, when a similar power supply was applied. This design advantage will be discussed in the next section. Furthermore, the influence of this temperature profile on the methane conversion is given in the next section as well.

3.6 Reactor design improvements

This section includes the reaction design improvements, for higher methane conversion in the GAP reactor.

The initial GAP reactor, which was used for plasma characterization with pure nitrogen, had 6 tangential inlets with the diameter of 1 mm. The geometry was based on [162]. The choice of the inlet diameter was not explained, therefore, the gas flow and the vortex formation was not justified previously.

During the initial experiments with 1 mm inlet diameter, the phenomena of the anode spot was observed. At the applied 100 mA current and 10 l/m nitrogen flow, the melted metal spots on

3. GAP Reactor results and discussion

the anode surface near the gas entrance were observed [159]. This anode spot caused the metal erosion, making it difficult to sustain the arc for longer time due to short-circuit.

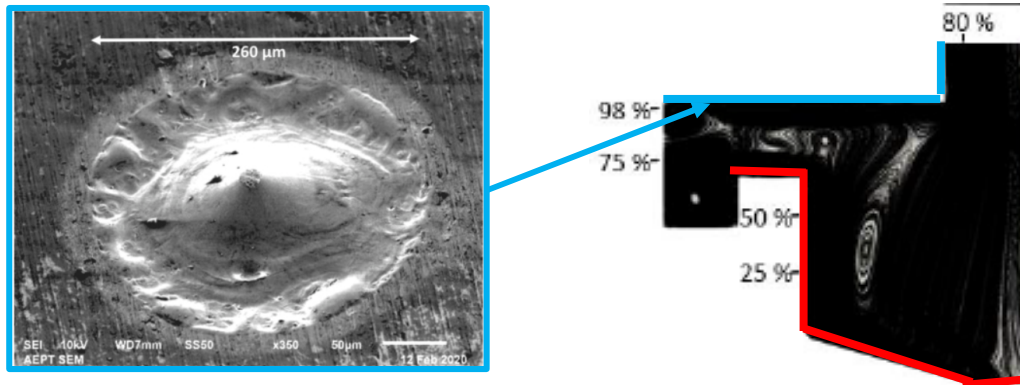


Figure 3-20 The anode spot and its location in the reactor [159].

The anode spot was created when the arc stayed in one location long enough, instead of “jumping”. The theory was that the anode spot resulted from the interaction of the local magnetic field and vortices, which “trapped” the arc in one place [159].

To check the theory, the gas flow simulation in 3D was done, to observe if the vortices were created at the location of the anode spots and could become the cause of the anode spot. The simulated velocity profiles and the streamlines were analyzed. Figure 3-21 shows the original geometry and the 3 other variations with various tangential inlet diameters. The simulated diameters were 1.5 mm, 2 mm and 0.75 mm. The fluid flow was simulated with k- ω -SST turbulence model, and without gliding arc.

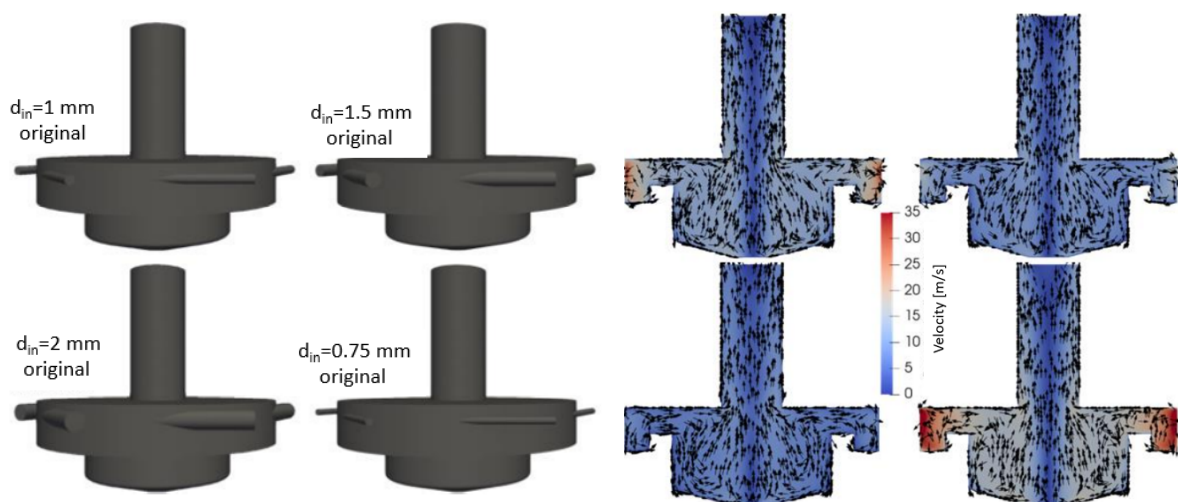


Figure 3-21 Velocity profiles and magnitudes for different tangential inlet diameters at 10 l/min methane flow.

Figure 3-21 shows that the highest velocity magnitude, and the turbulence respectively, was at the gas inlet, where the gas went through the smallest area. As expected, the lowest gas

velocity was at the center of the vortex along the reactor outlet axis. Comparing the 4 given geometries, the highest turbulence was with the smallest diameter 0.75 mm. With this high speed from 0.75 mm and 1 mm inlets, the gas entangled in smaller vortices before creating the main reverse vortex in the middle of the cathode cap. Therefore, it was distinct that the anode spot could be generated locally, because the gliding arc was trapped in these eddies at the reactor inlets, instead of being guided to the reactor center.

When the original geometry with 1 mm inlet diameter, and the geometry with an enlarged diameter of 2 mm were compared closely, the advantage of the latter was clear. Figure 3-22 gives more insight into where the flow eddies from the higher gas speed were formed. For the geometry with 1 mm diameter, the swirl-like streamlines were visible in the smallest gap between the electrodes, where the arc was initiated. Whereas with the 2 mm diameter, the streamlines were significantly smoother. This implied that to push the arc into the reactor center and to allow it to stabilize there, the smoother velocity streamlines were more beneficial.

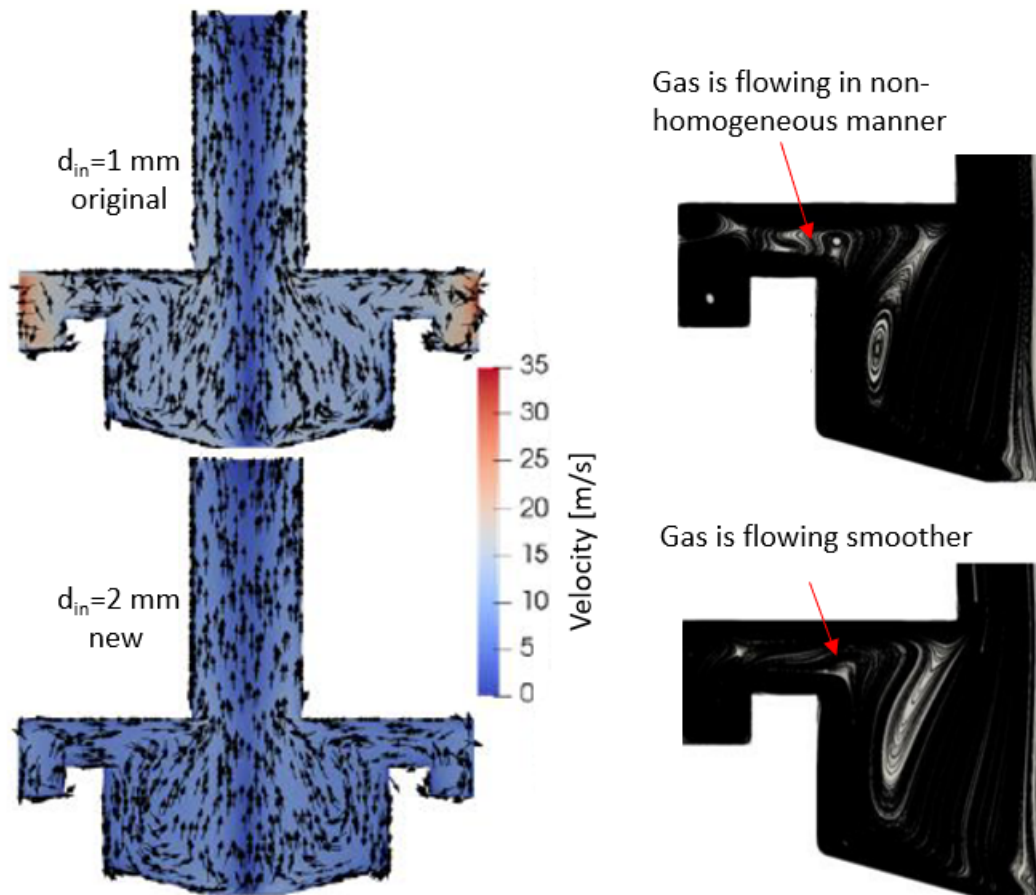


Figure 3-22 Velocity streamlines comparison of 1 mm and 2 inlet diameters.

Figure 3-22 shows that when the inlet diameter was increased, the velocity magnitude throughout the reactor was lower. This brought another advantage of the increased residence time. Thus, the methane molecules would have more time to interact with the arc. When the

3. GAP Reactor results and discussion

arc was stabilized and not broken immediately due to short-circuit, it moved inside the reactor for an extended time and heated up the gas. The simulated temperature plot of the “artificial” arc in Figure 3-23 gives an understanding of the temperature change of the gas surrounding the arc. The “artificial” arc in this simulation was raised to 1000 K, and the simulation was performed with argon for the simplification. The top view in Figure 3-23 (b) shows a trail of elevated temperature behind the arc. Even with 1000 K in the arc, the gas beyond it could be as high as 500-900 K. The temperature distribution contour plot in Figure 3-23 (c) represents the temperature change in volumetric dimension.

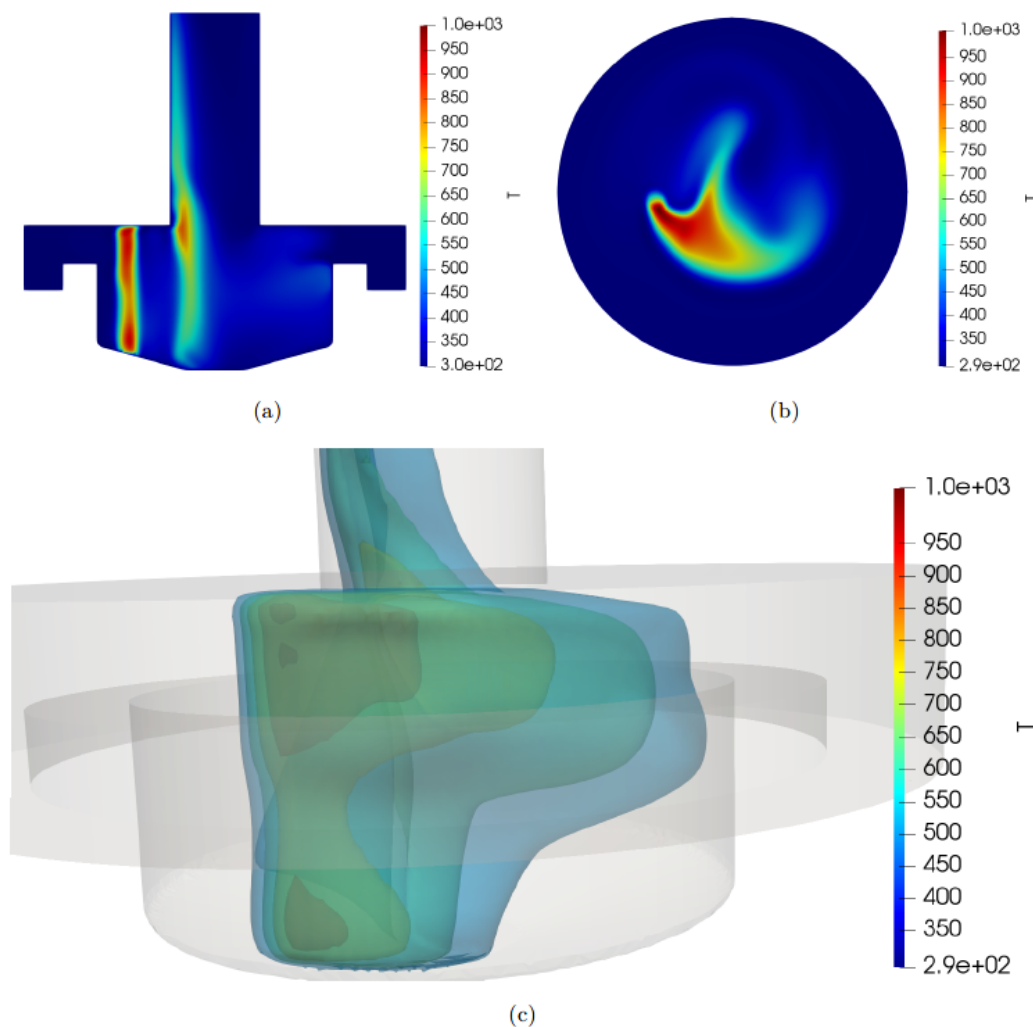


Figure 3-23 Side (a) and top (b) temperature [K] profile and the contour plot (c) at 500, 625, 750, 875 and 1000 K after 2.5 ms simulation with argon gas.

Consequently, if the arc moved over a larger volume inside the reactor, it could heat up a greater portion of the effluent gas. As it was discussed before, the thermal reactions convert methane into hydrogen at several thousand Kelvin temperatures. Thus, with the larger inlet diameter and resulted lower gas velocity, the arc was more stabilized and moved more towards the middle of the reactor and was ignited for the prolonged time. And additionally,

with more contact time between methane and the arc, due to the lower gas velocity, the conversion of methane could be increased.

Another alteration of improving the arc stability through the reactor geometry, was evaluating the functionality if the “step” of the reactor. Figure 3-3 shows the inlet chamber between the gas inlets and the reactor main body. This part of the reactor was thought to be a vortex generator [55].

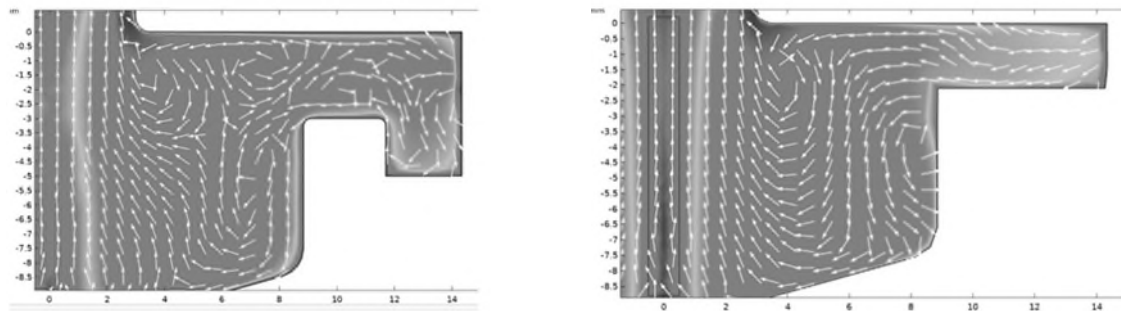


Figure 3-24 2D side view of the velocity streamlines of the original geometry (left) and altered geometry (right) without outer ring “step” for vortex generation, both with 2 mm inlet diameter.

When the tangential inlet diameter was increased to 2 mm, the eddies at the reactor inlet were still present as shown in Figure 3-24 (left). The original vortex generator outer ring “step” entrapped the gas, which entered the reactor with a high speed and created the local eddies in this reactor part. The previous experiments revealed the anode spots at the narrowest gap between the electrodes, hence, these local eddies contributed to these anode spots formation. After this “step” was removed, the gas velocity direction became more streamlined towards the reactor center as presented in Figure 3-24 (right). Hence, in the methane-argon experiments conducted at Ruhr-University Bochum, the GAP reactor geometries were built with the suggested alterations [88] [39].

Another geometry variation, which was suggested and successfully implemented for the better methane conversion, was the modification of the cathode cap.

3. GAP Reactor results and discussion

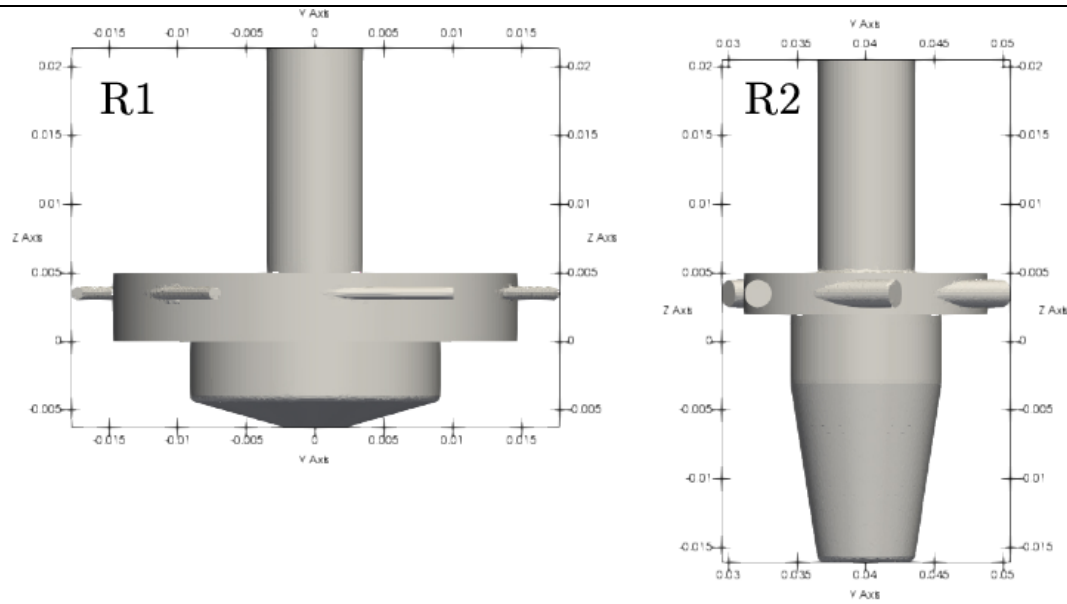


Figure 3-25 Cathode cap modification: R1 – original reactor, R2 – modified reactor.

Figure 3-25 shows another reactor design, which could improve the methane conversion. Namely, the increase of the residence time by enhancing the cathode cap length. The idea was that with the longer cathode cap, the length of the arc, respectively the reactive surface area, would be greater. Also, the gas velocity decelerated, since the distance that the gas travels from the tangential inlet to the reactor bottom was raised from 8 mm to 18 mm.

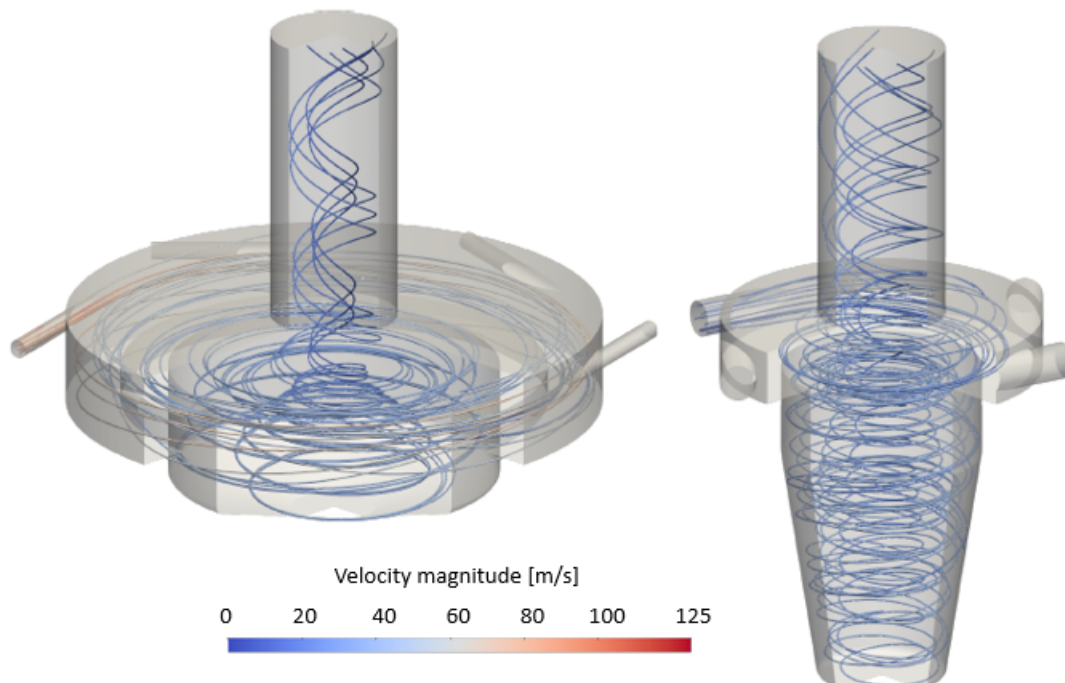


Figure 3-26 Velocity magnitude of R1 and R2.

Figure 3-26 shows that with the same 10 l/min inlet volumetric flow rate and with the same velocity magnitude scale, the modified R2 reactor exhibited a more homogeneous flow through

the reactor. The formed vortex in the R2 reactor was more concise, due to the narrower geometry of the reactor.

When velocity magnitude was compared from the top view, the gas turbulence was more prominent in R1 – the original geometry. The velocity gradients of the original geometry presented in Figure 3-27 (b) varied from 70 m/s at the vortex edges to 0 m/s at the vortex center. Whereas the R2 reactor design caused less steep velocity difference, hence, a more stable vortex was generated. This is visible in both the side and top view of the R2 reactor in Figure 3-27.

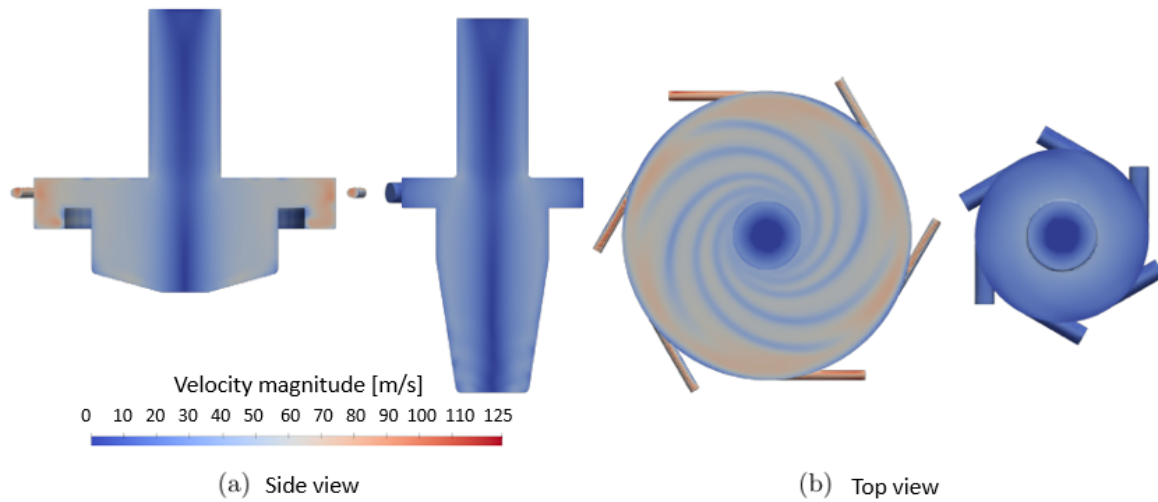


Figure 3-27 R1 and R2 reactors comparison in terms of velocity magnitudes.

When the “artificial” arc was applied, with the temperature of 4000 K, and the reactions set of CH₄-Ar was implemented, the temporary change in the temperature was observed as in Figure 3-28. The temperature magnitude was significantly higher for the modified reactor design R2. Whereas for the original reactor, the endothermicity of the reactions governed the temperature. Therefore, the temperature dropped drastically. The same temperature decrease was observed in the modified reactor, however, with more time the arc heated the gas starting from the bottom of the reactor, where the convective heat transfer was the lowest due to the low gas velocity.

3. GAP Reactor results and discussion

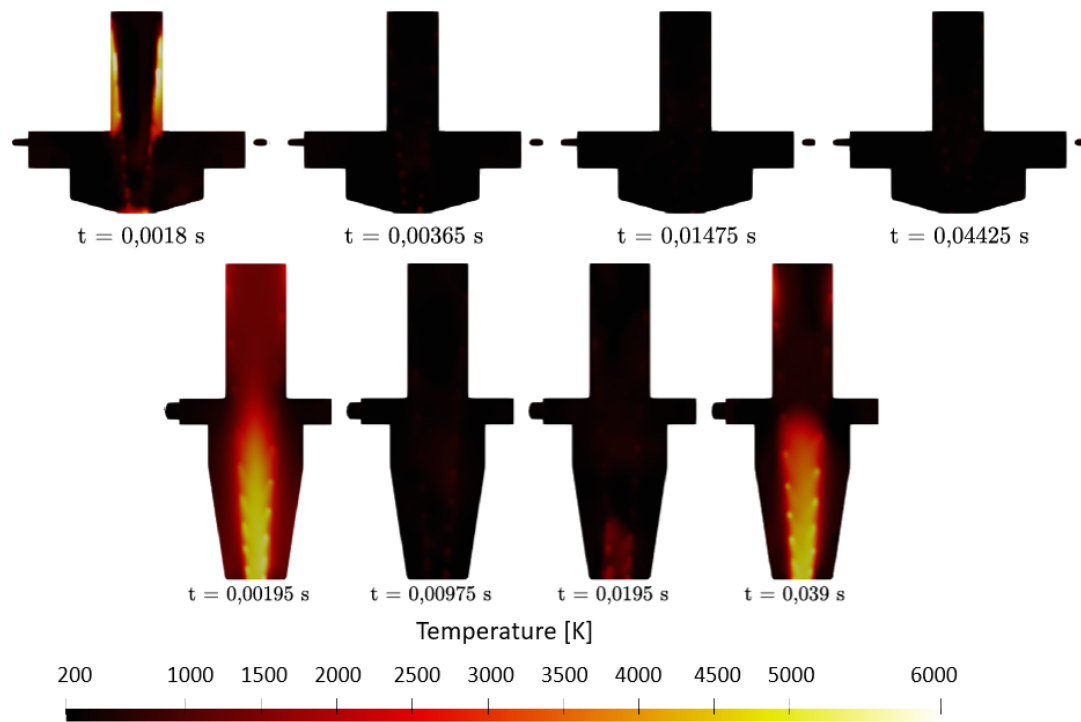


Figure 3-28 Temperature change with time for R1 (top) and R2 (bottom).

The notably higher velocity range of the original reactor impacted the temperature negatively, thus, the heat loss was stronger in the original reactor design. The experiments verified that the measured temperature at the arc with the original reactor design was 1490 K [163], and for the modified reactor design this temperature was significantly higher, at 6000 K [88].

The resulting products yields for the original and the modified reactors are presented in Figure 3-29 and Figure 3-30 respectively.

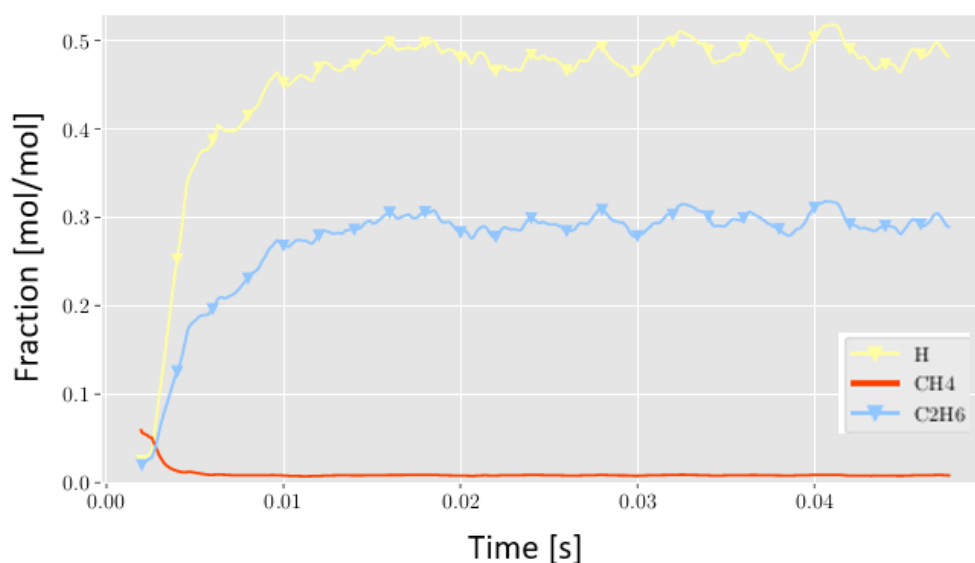


Figure 3-29 Product yields of R1 reactor, where C₂H₆ - main product.

In Figure 3-29 the main products were ethane, and H atom. This is explained with too low temperature achieved. Thus, the H atom remained unconverted.

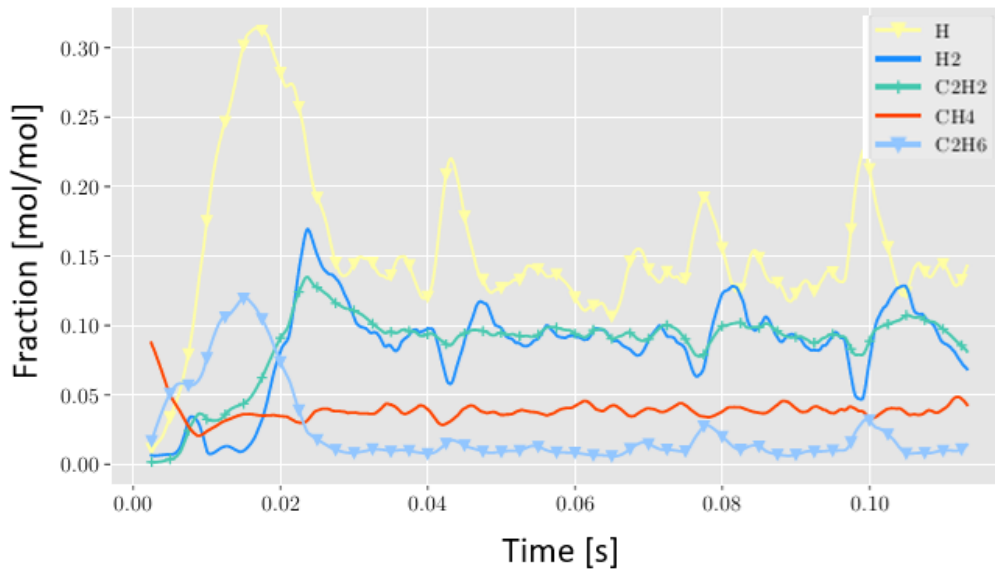


Figure 3-30 Product yields of R2 reactor, where H_2 , C_2H_2 - main products.

In Figure 3-30 the main products were the targeted H_2 and C_2H_2 – valuable by-product. This could be obtained due to a higher temperature inside the reactor.

In the experiments, no H atoms were measured by the analyzer, however, the modified reactor design showed the methane conversion improvement from 35 % to 44 % [39] [88]. Hence, it can be concluded that the heat distribution, the arc movement and the vortex flow in the modified reactor were helpful to increase the methane conversion.

3.7 Summary

The 0D model gave an understanding about the driving forces for the methane conversion in the gliding arc plasma. The simulation results showed that initially at the lower temperature the electron impact reactions generate methyl radicals, which afterwards react with methane and produce H_2 . However, due to the high temperature at the arc, the thermal reactions contribute to the methane conversion and override the electron-impact reactions.

The application of the 0D and 2D simulation identified the key features of the plasma, which were included in the 3D simulation. Therefore, the arc could be simulated as the artificial heat source, and lead to the similar results as in the experiments. The obtained results were used to modify the existing reaction geometry, and hence, increase the methane conversion by 9 %.

Moreover, the approach for the simulation of the GAP reactor was applied to the MW and SDBD reactor. This way a systematic methodology was utilized in the simulation of all reactors in this work, regardless of the type of plasma.

4. MW Plasma reactor

4.1 Introduction

This chapter gives the simulation results and the discussion of the methane pyrolysis in the microwave plasma reactor. The simulation was aided by the experimental setup, which included the windows for viewing the plasma. Also, the optical emission spectroscopy gave more information on the temperature profile of the plasma, which was used in the simulation model. Specifically, the 2D model could be more precise due to the location of the observation windows.

Similarly, as in the gliding arc plasma, the reaction set was refined with the 0D model. Then it was implanted in the 2D model. And finally the 3D model could be simulated.

The 3D simulation was compared to the experimental results, thus, the operating conditions for higher methane conversion and hydrogen selectivity could be optimized. This finding could benefit the future study.

4.2 Experimental setup

The experimental setup in the Ruhr University Bochum for the pyrolysis of methane with argon as the carrier gas is given in Figure 4-1. It involved a waveguide and quartz tube, where methane was transformed into the products. The magnetron generated 2.45 GHz microwaves and the power supply was varied between 0.6 and 6 kW [39]. The gases, which were detected at the outlet were CH_4 , C_2H_2 and C_2H_4 and the rest was assumed to be H_2 . The list of the gas analyzers was limited to these molecules since the 0D simulation showed a negligible concentration of C_3^+ and the heavier hydrocarbons.

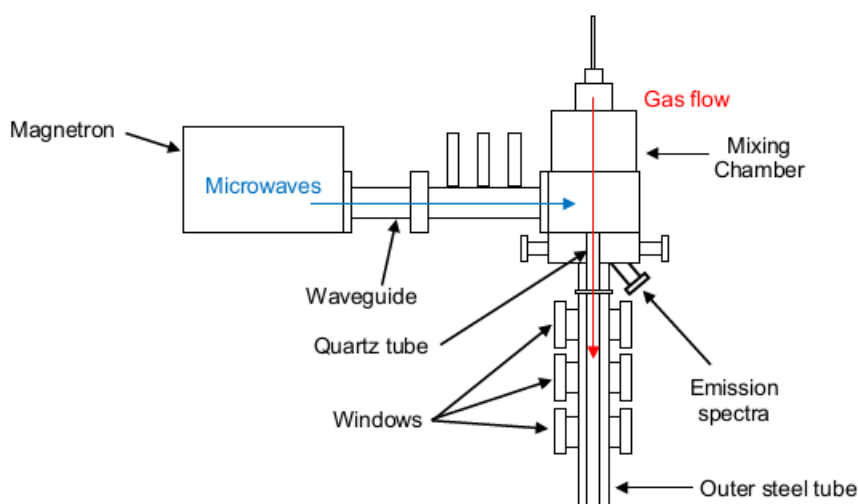


Figure 4-1 Experimental setup of the MW plasma reactor.

The schematic in Figure 4-1 includes the windows at the outlet tube, which were purposed for the observation of the spatial development of the microwave plasma. The shape and the size of the plasma was monitored, and the dependency on the power supplied and the CH₄-Ar mix content was observed. One of the examples of the MW plasma image is presented in Figure 4-2.

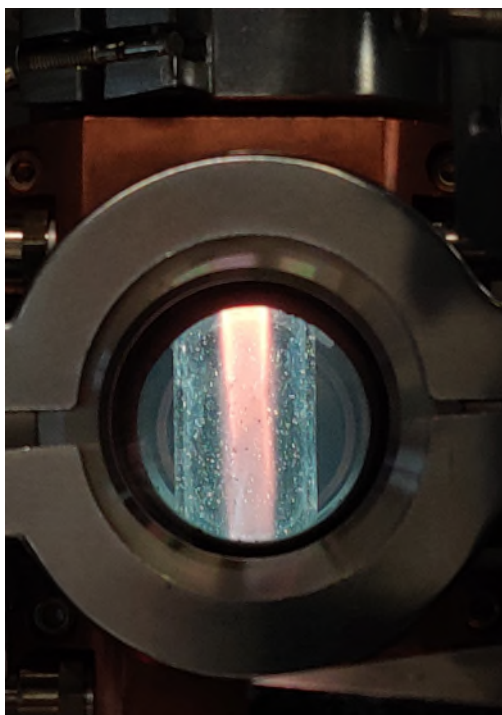


Figure 4-2 Photo of the MW plasma from the experiment in RUB [164].

The glowing light in Figure 4-2 is the MW plasma in the shape of the “plasma torch”. During the experiment the gas temperature was measured by the emission spectra of C₂, such as C₂H₂ and C₂H₄ and other species containing C₂. The measured emission spectra correspond to the Swan bands of the dicarbon molecules [73]. The Swan bands can help to identify the rotational temperature of C₂ molecules. The spectrograph measured the blackbody radiation from the dicarbon molecules. Thus, the measured temperature was around 4000 – 4300 K, see Figure 4-6 (a). Note that the glow intensity was the strongest at the waveguide, and the intensity was dissipated downwards in the direction of the gas.

In the following sections, the same simulation method as for the GAP reactor was applied, which included the combination of the measured gas temperature results and the imagery temperature profile of the plasma. In other words, the “plasma torch” was simulated as the heat source for the thermal methane conversion reactions.

To protect the quartz tube walls from the high temperatures radiated by the “plasma torch” and to enhance the methane interaction with the plasma, the gas mixture of CH₄+Ar was fed

4. MW Plasma reactor

through the tangential inlets. Figure 4-3 shows the reactor geometry where the gas entered through the tangential inlets and exited through the quartz tube.

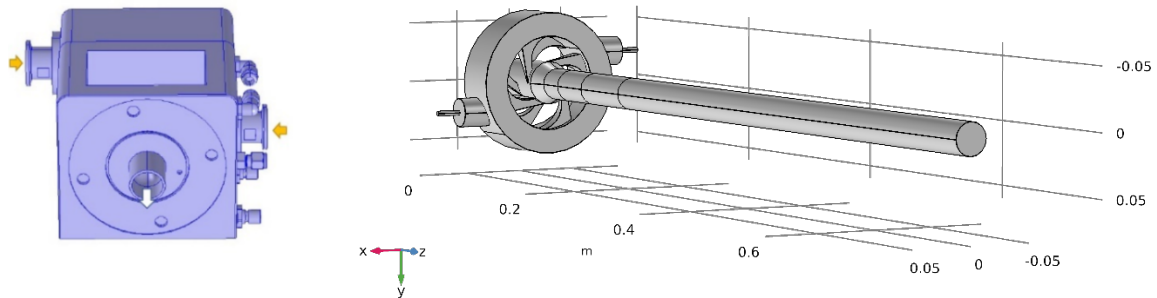


Figure 4-3 The mixing chamber with tangential inlets and the schematic of the full body of the reactor including the outlet tube.

The outlet tube had a diameter of 26 mm and a length of 0.74 m. The two inlet nozzles were at 3.6 mm in diameter. They were connected to the 8 flat-shaped flanges, thus, the gas entered the outlet quartz tube as a swirl.

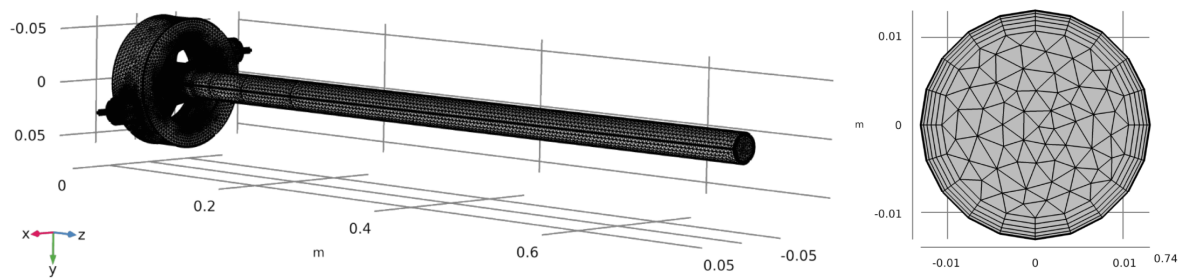


Figure 4-4 The auto-generated mesh of the 3D geometry and the cross-section view of outlet for 3D flow simulation without the plasma.

To simulate the reactor flow in 3D without the plasma and reactions interactions, the mesh containing ca. 1150000 elements and around 60000 boundary layer elements was used. It was the automatically generated mesh by Comsol Multiphysics®. For the flow simulation alone this generated mesh was sufficient, however, for the steep temperature gradients and the chemical reactions it was too coarse. Therefore, the mesh was adjusted to minimize the numerical error created by the mesh.

Figure 4-5 shows a mesh, which was more suited for the simulation. The mesh size was required to be fine to compute the fast reactions and high temperature more accurately. However, the fine mesh could not be applied throughout the whole reactor domain, because the computational power was limited. Therefore, the particular regions were with the fine mesh, and the rest was built with the coarser mesh. Normally, the time step should also be small enough, for the dynamic simulation to converge. However, in this 3D simulation, the time dependence was not observed, whereas 0D simulation was simulated over a time range. As

seen in Figure 4-5, the tube part, where the plasma torch took place, was built with the finest mesh, and resulted in more cells in the center. This was done, because most of the reactions occurred in the plasma torch. The region beyond the plasma was coarser, but still with the finer mesh in the tube center, since the temperature was still high in the middle. The rest of the quartz tube domain was built with a coarse mesh. The mixing chamber was less refined than in Figure 4-4. Because the velocity profile inside the quartz tube entrance was taken from the previously obtained fluid flow simulation with the mesh from Figure 4-4.

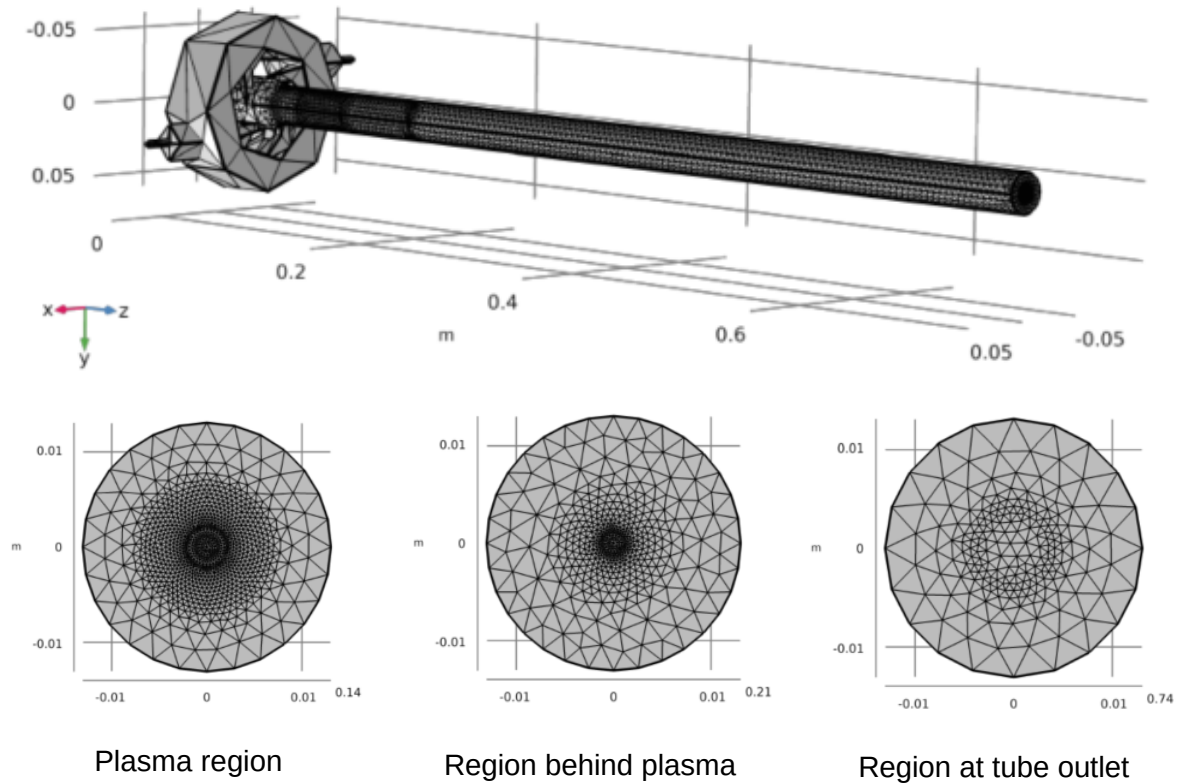


Figure 4-5 Final mesh for the plasma and chemical reactions simulation.

The mesh in Figure 4-5 contained around 1829000 elements, with 12600 boundary layer elements.

The simulation results were then compared to the experimental ones. The parameters which were compared included the temperature, methane conversion and ethyne selectivity, which are shown in Figure 4-6. The hydrogen was analyzed by the thermal conductivity sensor assuming that the gas contained $\text{H}_2/\text{CH}_4/\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{Ar}$. Whereas, CH_4 , C_2H_2 and C_2H_4 molecules were detected by the gas analyzer directly. Therefore, the hydrogen selectivity was not compared to the simulation results, since the precision of the measurement was lower than for the other species. Instead, the methane conversion and ethyne selectivity were used for the comparison. During the experiments only the traces of C_2H_4 were detected. Hence, the ethene selectivity was not used for the comparison.

4. MW Plasma reactor

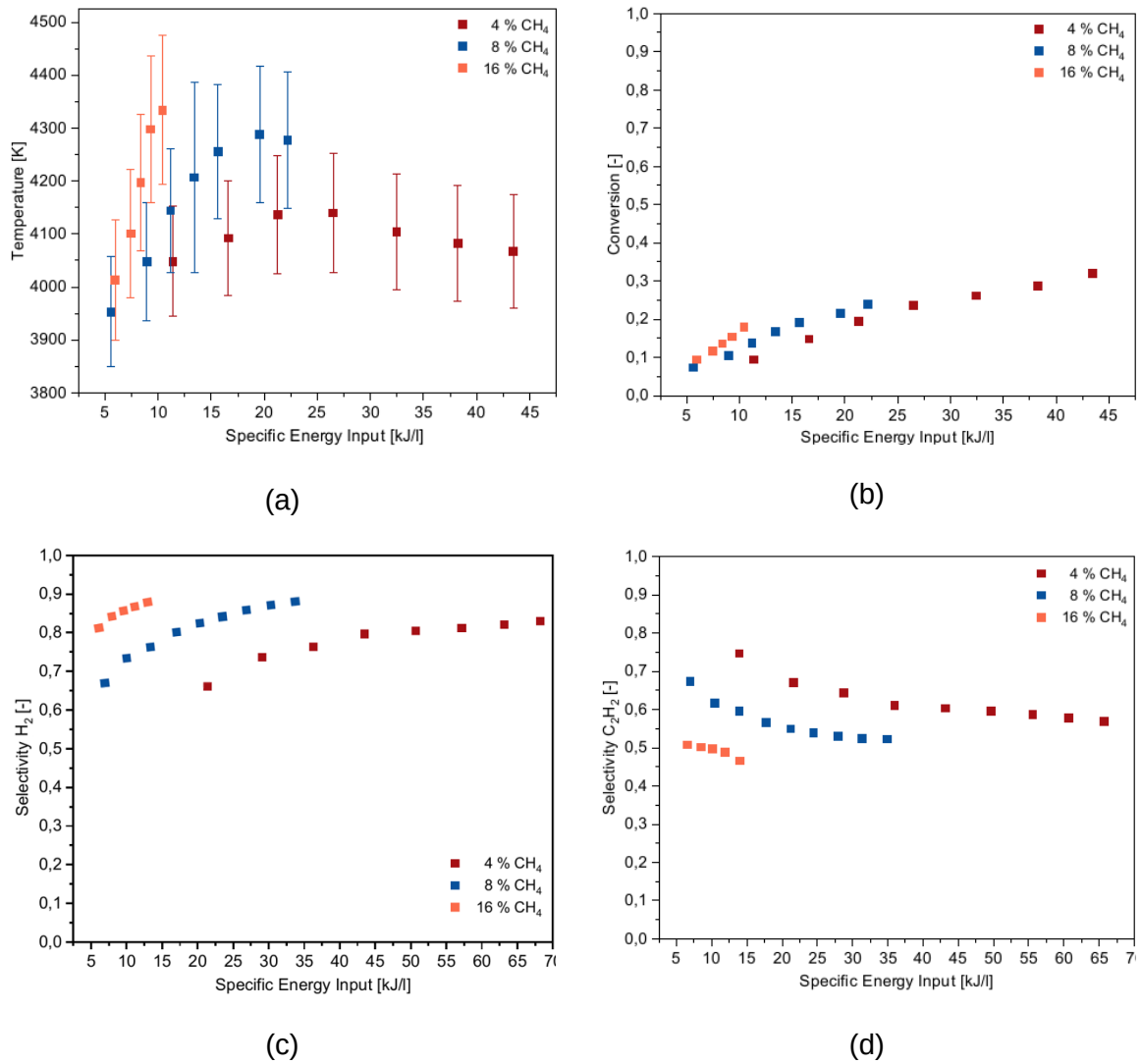


Figure 4-6 Experimental results with 1 – 16 vol% CH₄ in feed at 70 l/min at varying power supply: (a) measured gas temperature, (b) CH₄ conversion, (c) H₂ selectivity, (d) C₂H₂ selectivity.

The graphs in Figure 4-6 were plotted against the specific energy input SEI. It is equivalent to the power supply to the plasma, Q_{in} , and is calculated as follows:

$$SEI = \frac{Q_{in}[W]}{CH_4[vol\%] \cdot \dot{V}[l/min]} \quad (4-1)$$

Figure 4-6 (a) presents the gas temperature dependence on the CH₄ content in the feed gas and the applied power. The gas temperature was found through the rotational temperature measurement of dicarbon. This temperature was obtained by the optical emission spectroscopy during the experiments [73]. Assuming the rotational temperature and the gas temperature were equal, the highest temperature in the “plasma torch” was established and depicted in Figure 4-6 (a). As it was expected, the lowest measured temperature was at the lowest SEI. The gas mixture with the highest methane content of 16 vol% revealed the highest

gas temperature throughout the whole span of the applied SEI, which increased from ca. 4000 K to 4350 K. In contrast, the gas temperature increase was the smallest between ca. 4050 K – 4150 K for the gas with the lowest methane in the mix, where only 1 vol% on CH₄ was present in the feed gas. This can be explained by the thermal conductivity difference of argon and methane, at 300 K they are 17.9 mW/m·K for Ar and 34.19 mW/m·K for CH₄ [165]. In other words, it is easier to heat up methane than argon, therefore, when the power supply is increased, the gas containing more methane achieves higher gas temperatures than the gas with more argon. The emission intensity was observed in the axial and the radial direction of the quartz tube, thus, temperature change along the tube and the radial temperature profile were obtained.

Figure 4-6 (b) shows the conversion achieved for the different CH₄+Ar mixtures. Similarly, as in the GAP reactor, the lower CH₄ content in the feed results in the higher conversion. As it was explained before, the plasma ignition and sustention were easier with inert gases such as Argon. Hence, when CH₄ was more diluted, the supplementary plasma energy was available for its conversion. Whereas, the presence of methane at a greater concentration meant less plasma carrier gas Ar in the feed, thus the plasma energy was lower, because Ar was the main contributor to the plasma generation. However, to achieve the same conversion level, less SEI was required for when CH₄ was present at a higher concentration. The energy efficiency was higher, since more CH₄ molecules were in the inlet gas and were readily available for the reaction. The maximum conversion achieved was 30 % for the 4 vol% CH₄ gas mixture

Figure 4-6 (c) and (d) are the hydrogen and ethyne selectivities. H₂ and C₂H₂ selectivities were reversely proportional depending on the methane content in the feed gas. The highest achieved hydrogen selectivity was 85 % for the feed gas containing the highest methane concentration. This occurred because H₂ participated in the side reactions. Therefore, when the concentration of CH₄ was higher, the rate of hydrogen production was greater than the consumption amount. Consequently, the higher selectivity towards hydrogen resulted in the lower production of the by-product ethyne. Hence, the selectivity of C₂H₂ was the greatest, when the selectivity of hydrogen dropped, which resulted in a higher rate of conversion of methane. When methane pyrolysis follows the Kassel mechanism, ethyne is the final product before the soot formation and hydrogen production [48]:

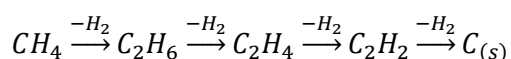


Figure 4-7 shows the gas analysis during the experiments. Here the gas flow rate was 40 l/min, which was lower than in the experimental results discussed above. Therefore, the methane conversion was higher than in Figure 4-6 (b). And as it was observed previously, the

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H₂ selectivity was greater when methane content in the feed was changed from 2 vol% to 4 vol%.

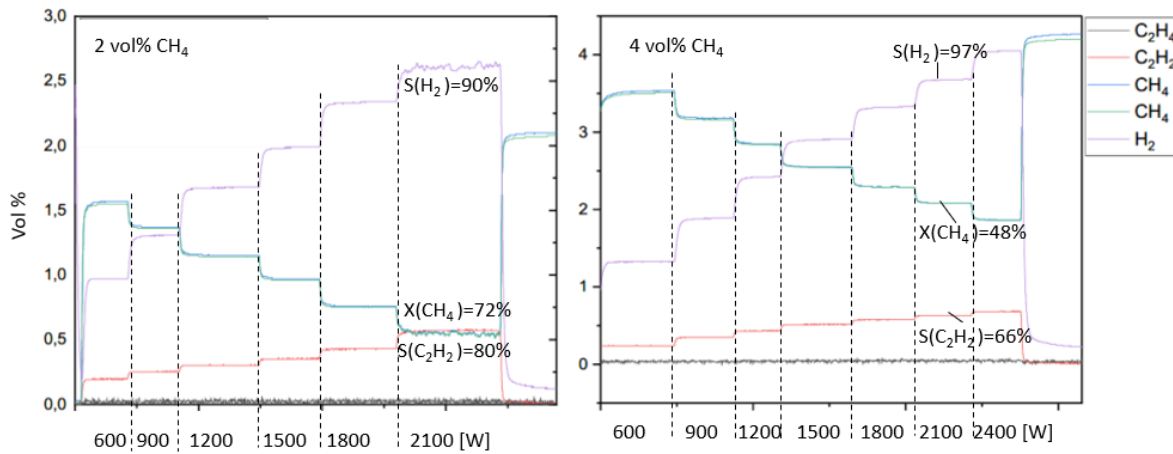


Figure 4-7 Online gas analysis for 2 vol% (left) and 4 vol% (right) CH₄ in feed at 40 l/min with increasing power supply.

Figure 4-8 shows the images of the MW plasma development by varying the power supply and the gas content together with the flow rate. At the higher methane concentration, the plasma shape was narrower and more intense in the center. Thus, the gas temperature was greater with more methane in the feed, due to the concentrated shape of the plasma. The gas flow rate did not seem to have an influence on the gas temperature. The optical emission spectroscopy also demonstrated almost identical gas temperatures, when the same power was applied for the same gas composition at different volumetric flow rates [166].

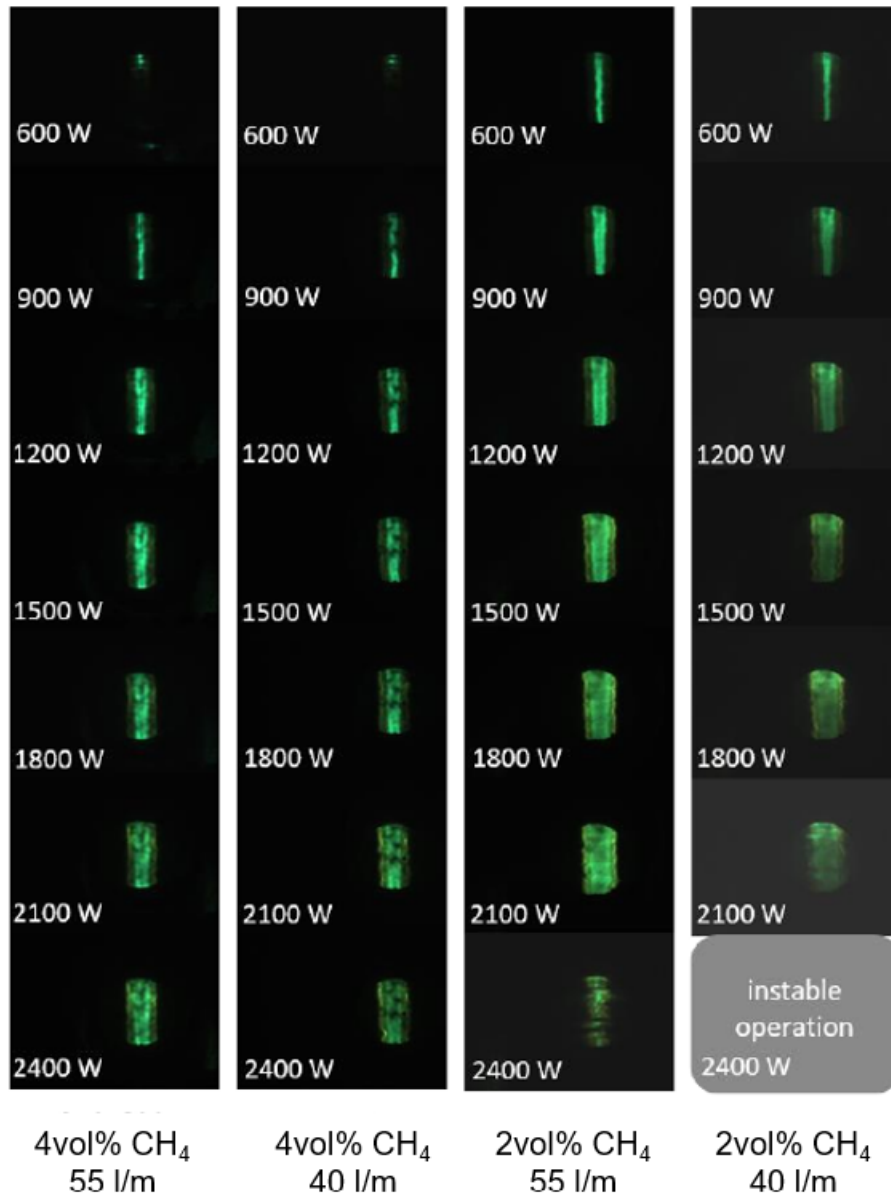


Figure 4-8 Optical representation of MW plasma at 2 vol% and 4 vol% methane and 40 l/min and 55 l/min gas flow at increasing power supply, green color from white balance filter [164].

These experimental results were used for tuning the simulation and the validation.

4.3 “Plasma torch” as a heat source

In the previous chapter, the plasma arc in the GAP reactor was simulated as a heat source. This adjustment allowed for the 3D simulation to converge, even though the several hundred reactions and the steep velocity and temperature gradients were connected.

To check if the application of the plasma as a heat source had an impact on the product yields a 0D simulation was performed. The full reaction set (F) and the thermal reactions (T) were compared in Figure 4-9. The full reaction set contained both thermal and electron impact

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reactions, in total 274 reactions and 34 species [94] [96]. Whereas the thermal reaction set included 157 reactions.

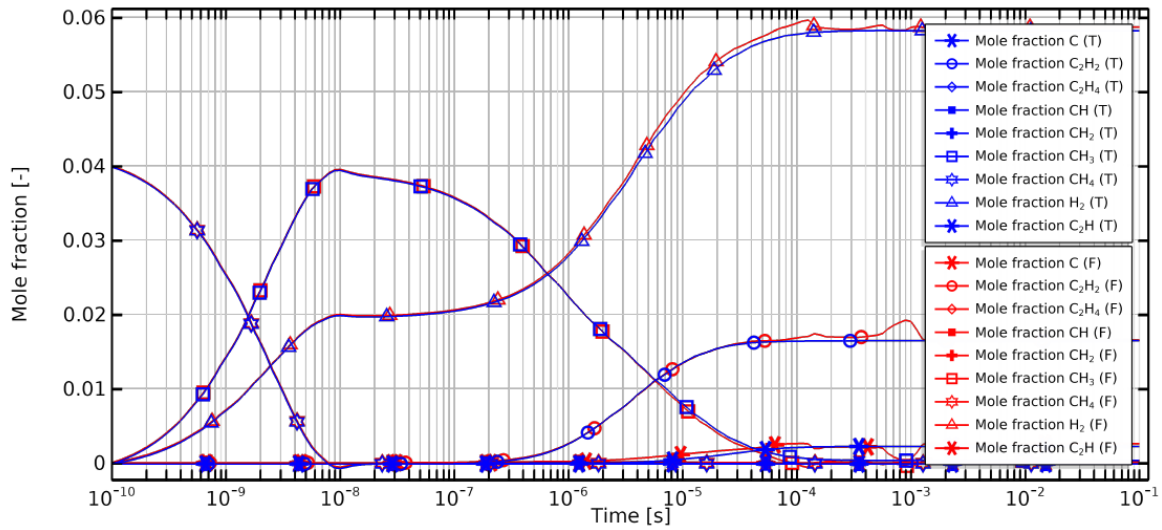


Figure 4-9 0D simulation for 4 vol% CH₄+Ar mix at 70 l/min at 3000 K, for the full reaction set (F) and thermal reaction set (T).

From Figure 4-9 it could be noticed that CH₄ was fully converted at 3000 K. Moreover, the produced amount of H₂ and C₂H₂ was almost identical for both reactions set. Hence, the exclusion of the electron impact reactions did not influence the results, since at such high gas temperature the thermal reactions were the significant ones.

Upon the further analysis, C₂H₅, C₂H₆, C₂, and C₂H species could also be omitted, because the amount of these species was almost zero at 3000 K and higher temperature. The reduction of 4 species shortened the reaction set by 44 reactions, resulting in 113 reactions. The discrepancy of H₂ and C₂H₂ mole fractions between both reaction sets in Figure 4-10 was minor. These refined reactions were used further in the 3D simulations.

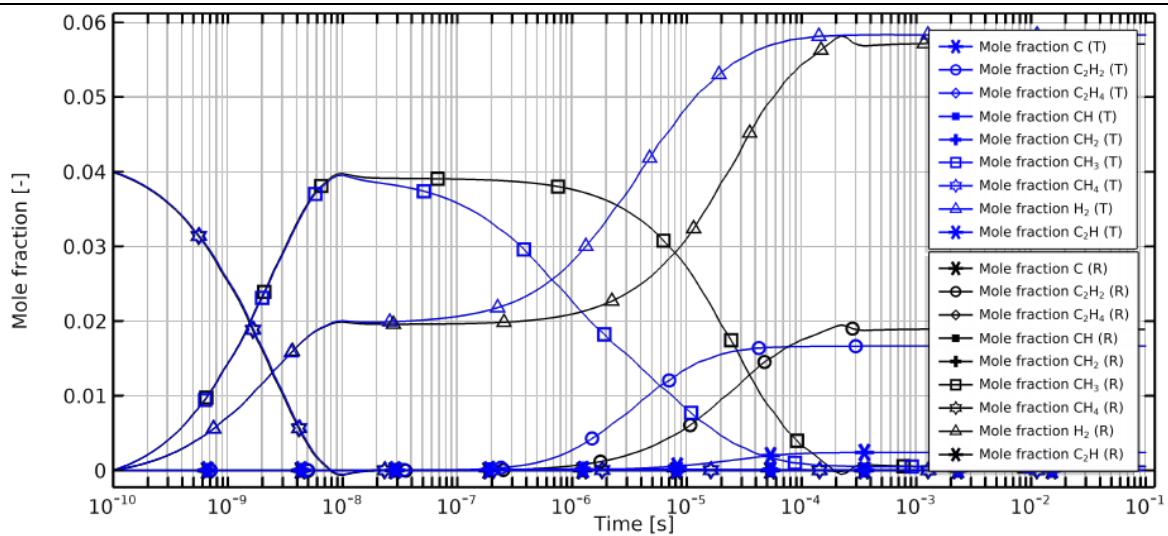


Figure 4-10 0D simulation for 4 vol% CH₄+Ar mix at 70 l/min at 3000 K, for the full reaction set (F) and reduced reaction set (R).

In order to simulate the “plasma torch” as a heat source, the suitable correlation between the observed shape of the plasma and the measured temperature was required to be established. The correlation should be dependent on the applied temperature. The plasma glow, which was observed from the photos, and the optical emission spectroscopy indicated that the temperature profile had a Gaussian distribution form as shown in Figure 4-11. Figure 4-6 (a) revealed that when the power input increased by several times, the temperature did not increase at the same rate. The power increase made the plasma volume larger and distributed the hot gas regions across a larger area. Hence, the distribution was broader with the increasing power input.

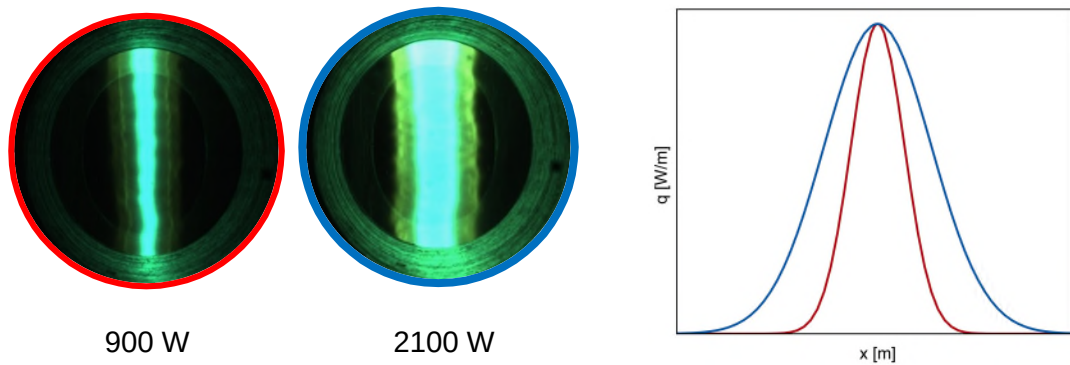


Figure 4-11 Gaussian distribution of the applied power in the plasma at 900W and 2100 W for 4 vol% CH₄+Ar mix at 70 l/min.

The expression used to describe the power supply, which was then assumed as the heat source for the reactions is given in Equation (4-2):

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$$q_{plasma} = Q_{supply} \cdot \frac{1}{2\pi \cdot \sigma^2} \cdot \exp\left(-\left(\left(\frac{x^2}{2 \cdot \sigma^2}\right) - \left(\frac{y^2}{2 \cdot \sigma^2}\right)\right)\right) \cdot \frac{1}{z_L} \quad (4-2)$$

$$\sigma = \frac{r}{\sigma_{DF}} \quad (4-3)$$

where z_L is the length of plasma torch equal to 0.043 m, r is the outlet tube radius, Q_{supply} is the power supplied, σ is the standard deviation, σ_{DF} is the distribution factor, x, y is the directions in 2D plane. The temperature profile, which was approximated to the Gaussian distribution shape in Figure 4-11, was limited by the quartz tube dimensions, namely the radius and diameter. Therefore, the standard deviation σ used for the temperature profile approximation was linked to the tube radius r , which is given in Equation (4-3). The tuning parameter σ_{DF} , the distribution factor, was adjusted case by case to match the simulated and the observed temperature profile, which was used further for the 3D simulation of the reactions. Afterwards, the reactions set was adjusted again when the model expanded from 0D to 3D, since, the methane conversion and ethyne selectivity were compared to experimental results.

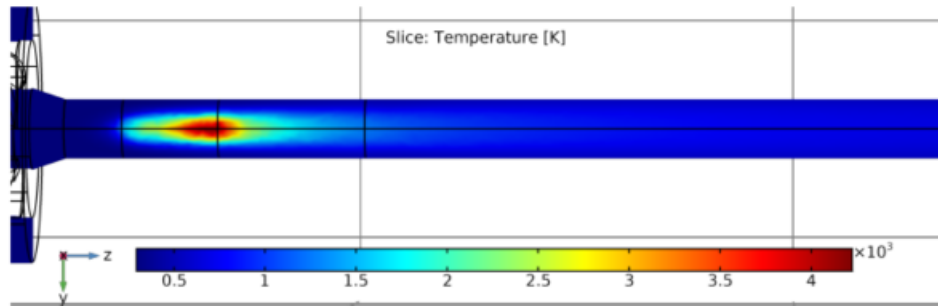


Figure 4-12 Temperature of the MW plasma as a heat source for 4 vol% CH₄+Ar mix at 70 l/min without reactions.

Figure 4-12 shows the achieved temperature profile when the plasma was substituted by the heat source with the Gaussian distribution. Similar to the images from the laboratory, the hottest area was at the source of the plasma and in the middle of the quartz tube, where the velocity magnitude was the lowest. The inlet chamber created the gas vortex flow along the quartz tube, which protected the quartz tube walls from overheating by the convection. Also, the temperature outside of plasma was close to the ambient, which was also observed in the experiments. In this simulation at Figure 4-12 only the gas flow and heat transfer equations were included, without any reactions taking place. Therefore, $Q_{supply} = 500$ W was sufficient to achieve 4200 K gas temperature. Whereas in reality around 1000 W power was applied. It can be explained by the fact that Ar is a light molecule (see Figure 2-12), and it can be heated

easily. Moreover, the methane pyrolysis is highly endothermic, therefore, when simulating the plasma reactors, the reaction enthalpies must not be excluded.

Figure 4-13 gives the outlook of the distribution factor σ_{DF} . The distribution factor and the standard deviation for the Gaussian distribution were reversely proportional. Hence, when the power supply increased along with the gas temperature, the calculated distribution factor became higher.

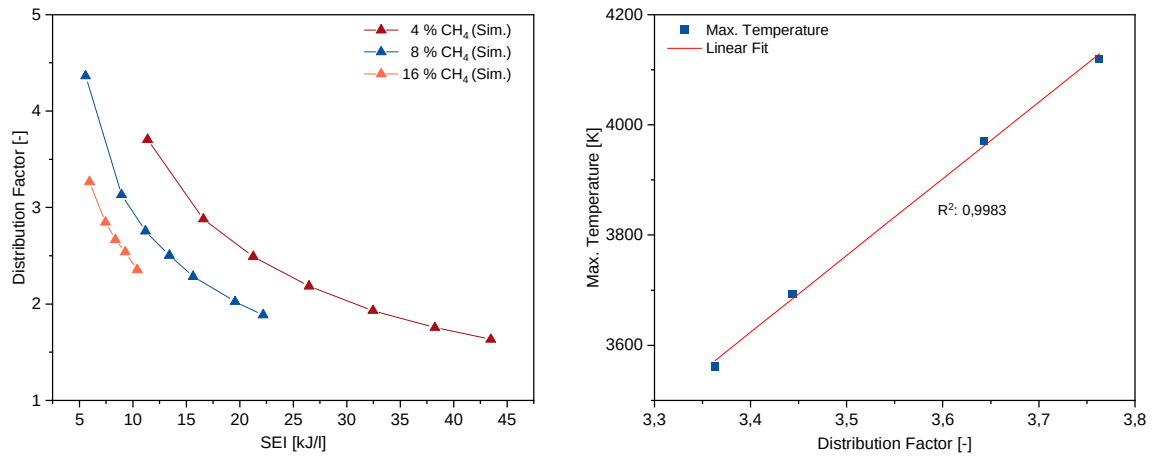


Figure 4-13 Distribution factor adjustment for various power supply.

The correlation found in Figure 4-13 could be used for other methane concentrations in a similar manner. Figure 4-14 presents the simulated and experimental results for the gas temperature. The simulation was performed in 3D and included the chemical reactions. The greatest difference between the simulated and experimental value was 100 K, which was acceptable considering the temperature magnitude.

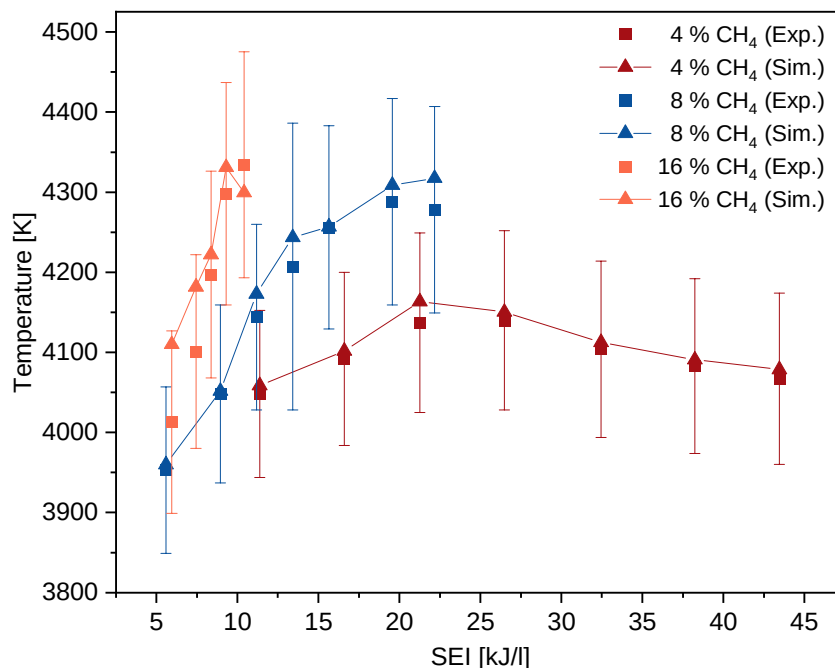


Figure 4-14 Simulated and experimental of the gas temperature.

Therefore, the modeled heat source was employed in the next steps of the simulation. Where the fluid flow and the chemical reactions were included in the simulation.

4.4 3D fluid flow simulation

Initially, to gain the knowledge about the flow behavior, and the influence of the plasma heat on the flow, the fluid flow and heat transfer were simulated in the whole reactor, without the inclusion of any reactions. And in the next step, the obtained velocity and temperature profiles at the quartz tube entrance were used as the initial conditions, and only tube part was simulated for the reactions. This approach saved the computational time.

Figure 4-15 represents the streamlines obtained at the different volumetric flow rates: 50 l/min, 70 l/min, 90 l/min, 110 l/min excluding the reactions or the artificial heat source. Although, the experimental results were all conducted with 70 l/min, comparing the fluid flow at different flow rates gave an insight about the optimal conditions. The inlet nozzles were shaped specifically to create the vortex flow, so that the quartz tube could be protected from the high temperatures at the plasma location, and that the gas and plasma could be interacted better due to enhanced mixing. As gas velocity increases, heat resistance at the quartz walls also increases. However, this comes at the cost of the reduced residence time, which can negatively impact methane conversion efficiency.

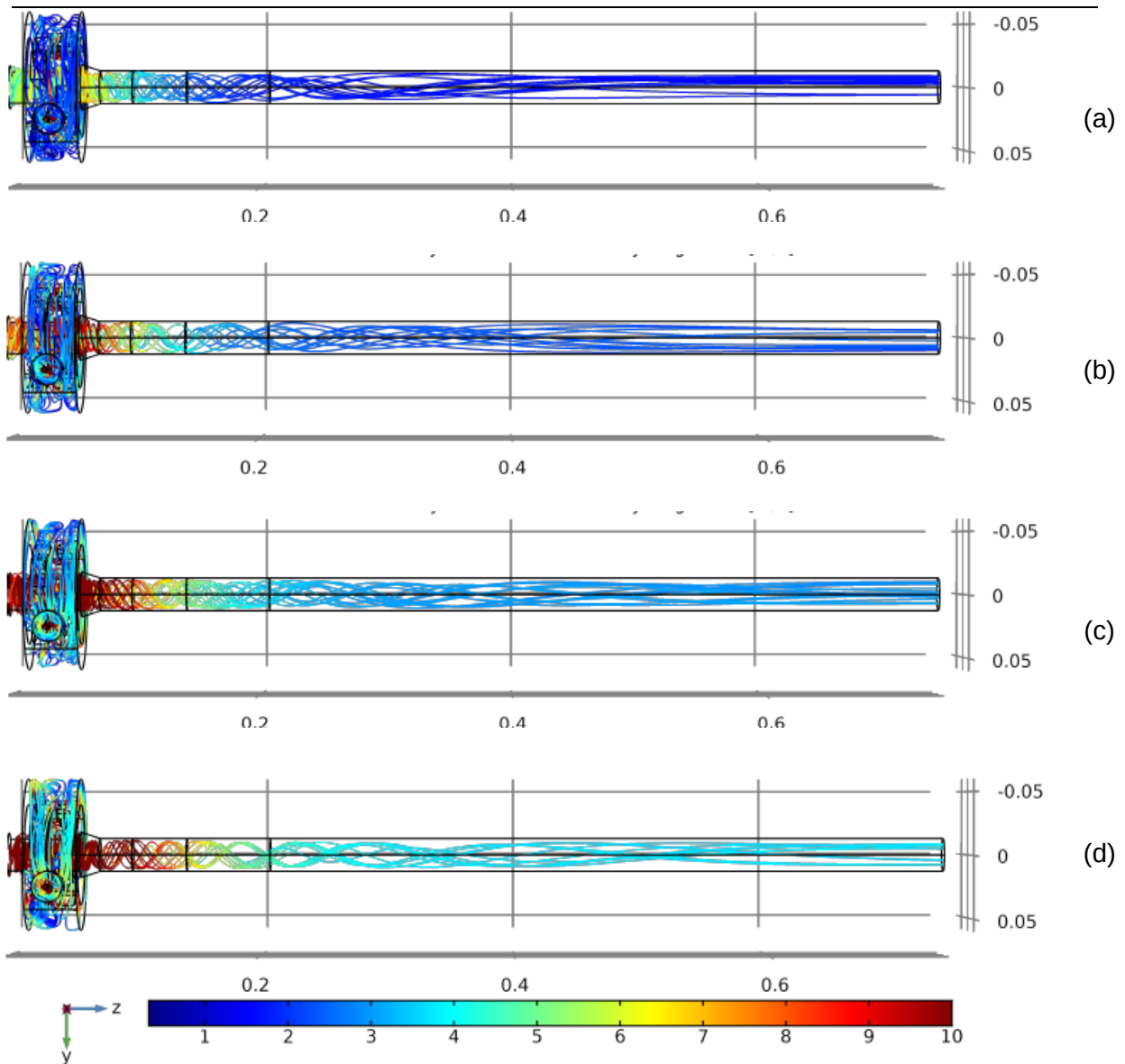


Figure 4-15 The 3D simulation fluid flow velocity streamlines at ambient conditions with varying volumetric flow rates (a) 50 l/min, (b) 70 l/min, (c) 90 l/min, (d) 110 l/min.

The streamlines at different flow rates showed that the vortex flow was developed in the mixing chamber and spread to the quartz outlet tube. The distance at which the vortex flow was maintained was the greatest at the highest simulated flow rate 110 l/min. In case of a lower inlet flow rate, as shown in Figure 4-15 (a), the vortex dissipated already at around 1/3 of the tube length. Also, as expected, the velocity magnitude was directly proportional to the volumetric flow rate.

The plasma was ignited almost immediately after the mixing chamber, and in all of the simulated cases the gas still exhibited vortices at the walls. Therefore, even 50 l/min was enough to create the vortex and protect the walls from the hot plasma.

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Different velocities resulted in different contact time between methane and plasma. With the slower velocities, the reacting gas had more time to react. However, the drawback could be that when the gas was too slow, the carbon soot could be formed at the walls of the tube, instead of leaving the tube at the outlet. Figure 4-16 shows experimental methane conversions at different flow rates for 4 vol% CH₄ in the feed gas. The x-axis in the graph was standardized over the moles of CH₄, hence, the SEI is lower for 70 l/min than for 40 l/min for the same power input, since the number of moles of CH₄ is higher in the 70 l than in the 40 l flow.

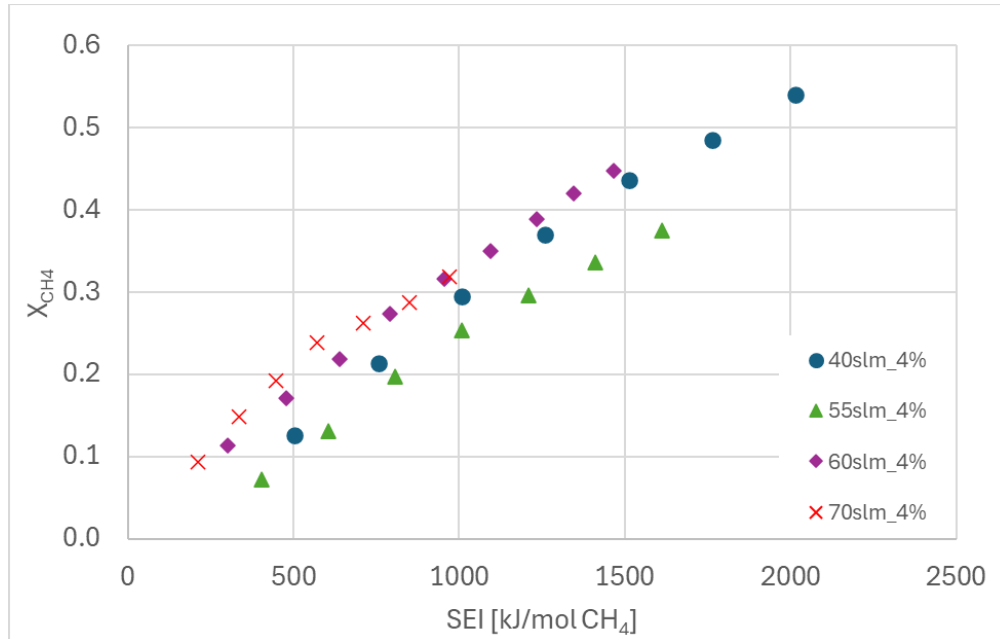


Figure 4-16 Methane conversions at 4 vol% CH₄ in feed at 40 l/min, 55 l/min, 60 l/min, 70 l/min.

The conversions in Figure 4-16 showed that the highest conversion of 55 % was at 40 l/min flow rate, and the lowest reached conversion was at 70 l/min. This was explained by the difference in the residence time through the quartz tube. Hence, one way to improve the conversion of methane was by lowering the volumetric flow rate of the feed gas. On the other hand, when the conversion of methane was compared at the SEI level, a greater conversion was achieved at the higher flow rate. Therefore, the energy efficiency was greater when more gas was flowing through the reactor. This trade-off between the energy consumption and the methane conversion can be considered further for the scale-up or numbering-up of the MW plasma reactor at the industrial scale.

Figure 4-17 shows the velocity streamlines after the application of the plasma as a heat source. There was a significant difference between the velocity magnitude in comparison to Figure 4-15. The gas temperature influence on the density was observed, thus, the velocity was higher at the greater temperatures.

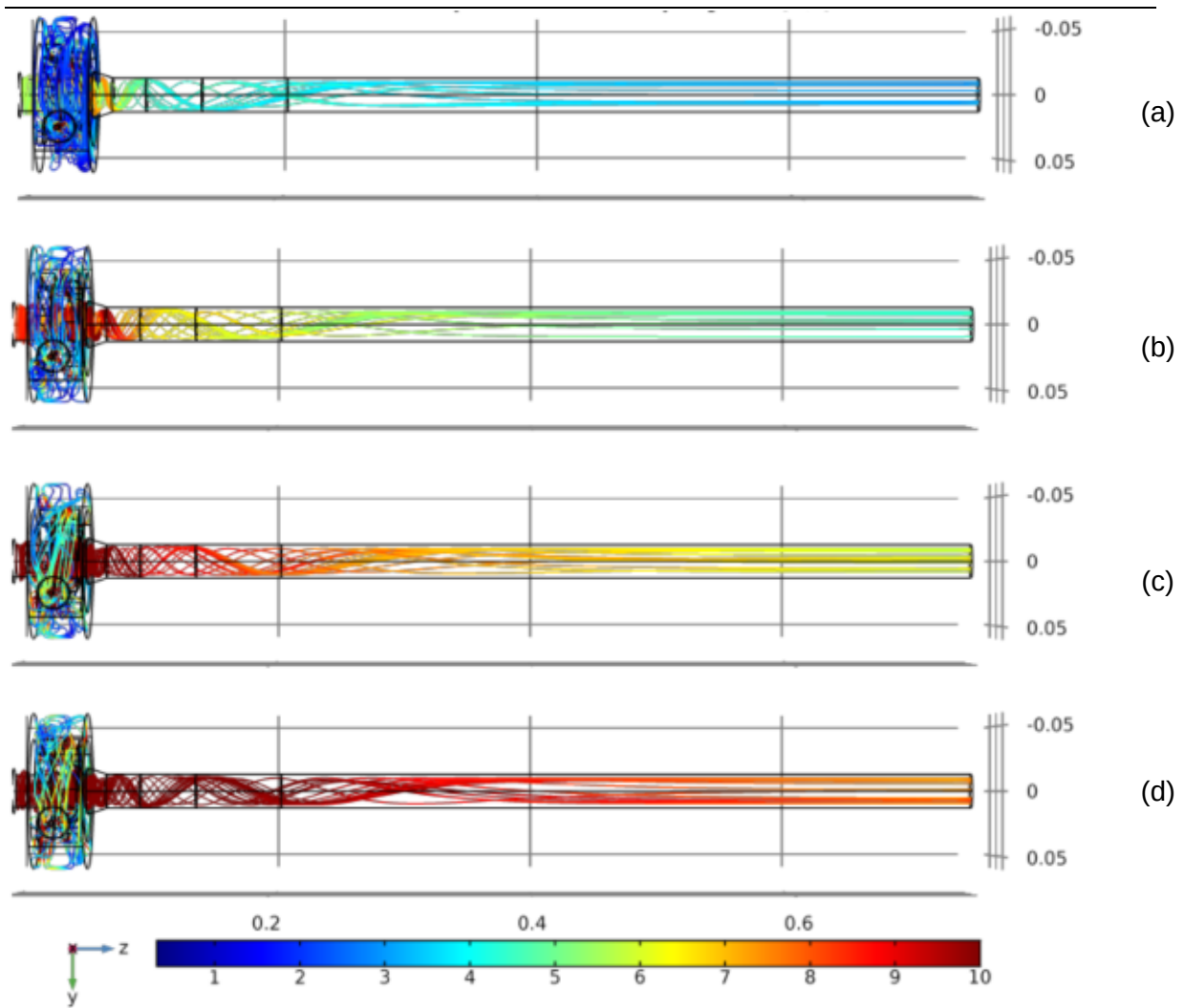


Figure 4-17 The 3D simulation fluid flow velocity streamlines with applied heat source at varying volumetric flow rates (a) 50 l/min, (b) 70 l/min, (c) 90 l/min, (d) 110 l/min.

When the velocity profiles for isothermal and non-isothermal conditions were compared side by side, the effect of the heat source on the velocity was visible more prominently. Figure 4-18 presents the difference in the velocity magnitude.

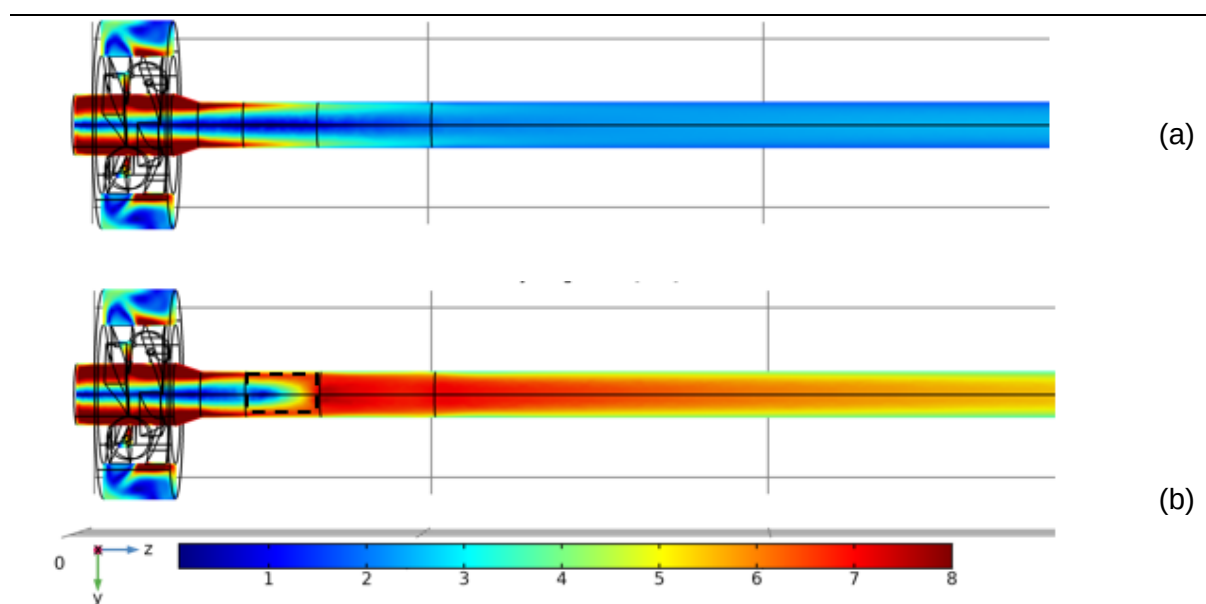


Figure 4-18 2D velocity profile (a) at ambient conditions, (b) with heat source marked with the dotted line.

When the gas was simulated with the isothermal conditions as in Figure 4-18 (a), the velocity gradient reduced gradually after the mixing chamber. On the other hand, when the heat from the plasma torch was introduced, the gas accelerated at the heat source. And the gas left the tube at a greater velocity.

This comparison revealed that the temperature gradients had a significant impact on the gas flow, and, consequently, on the methane conversion. Therefore, the temperature change in the simulation could not be neglected.

4.5 3D flow with chemical reactions simulation

This section presents the outcomes of integrating 3D fluid flow with the “plasma torch” as a heat source, alongside the chemical reactions derived from the 0D simulation.

Due to the simulation convergence issues, the reactions rates were reduced by 10^{-4} . Upon the further analysis, to lower the concentration of the radicals at the reactor outlet, the reactions where CH_3 and CH_2 radicals are produced were slowed down by 10^{-5} . This was necessary, due to a high concentration of the radicals at the tube outlet. The reactions, which followed the direct carbon production path $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{C}$ were only multiplied by 0.4 factor for the faster simulation convergence.

The rate constants can be modified iteratively, by tuning the reaction rate parameters and comparing them with the experimental data [167]. The reaction mechanism optimization strategy used in [167] and [168] was based on the polynomial expansion method, and the tuning of the reaction rates was required because the reactions were lumped into the reaction

classes. Due to lumping, the reaction kinetics of the individual reactions led to the discrepancies from the experimental results. The polynomial expansion method is a mathematical technique that expresses a random variable as a series of the orthogonal polynomials. The idea is to expand the output of a model, which is influenced by the uncertain inputs, in terms of these polynomials. In case of [167], the sensitivity analysis of the reaction rates was performed by the polynomial expansion method, and the results were compared to the experimental data. As a result, the reaction rates were multiplied by the calibration rate parameters [161]. However, this iterative tuning was performed on the 0D model, and it took 2 days to complete [161]. Therefore, as the reaction was simulated in 3D, the described iterative sensitivity analysis was not possible to perform, due to the intensive computational effort. Hence, the multiplication factors in this work were identified by the trial and error.

Figure 4-19 shows the temperature profile that is obtained from the simulation where the methane reactions were included. As identified by the 0D simulation, only the thermal reactions were included, and the plasma was replaced by the heat source. For the simulation with the reactions, a higher power input was required to achieve 4200 K than in Figure 4-12. Figure 4-19 had resulted from the power input of 1785 W, which is closer to the power applied during the experiments, than Figure 4-12, where no reactions were included. Hence, it can be remarked that most of the power supplied was transferred into the heat, which then drove the methane pyrolysis reactions.

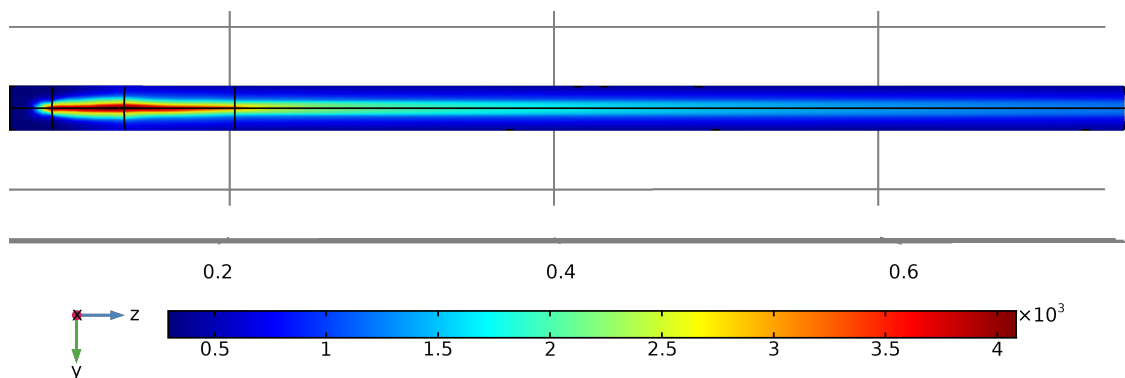


Figure 4-19 Temperature profile for 4 vol% CH₄+Ar mix at 70 l/min with reactions.

In comparison to Figure 4-12, the elevated temperature beyond the magnetron location was observed. The temperature of 1000-2000 K persisted along the entire length in the center of the tube. This could be explained by the reaction enthalpies. To check the theory, the reaction enthalpy profile was illustrated in Figure 4-20.

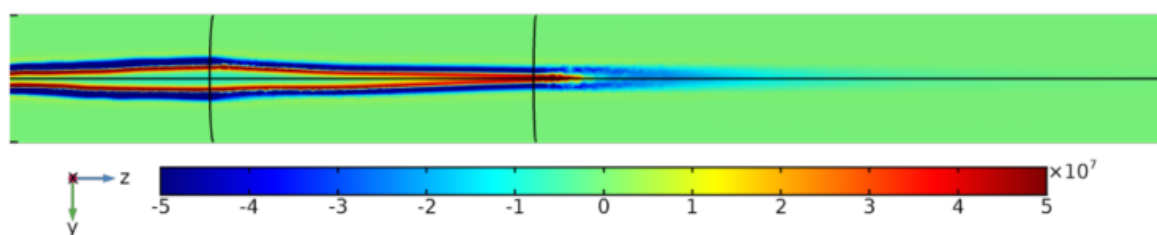


Figure 4-20 Reaction enthalpy at the plasma.

Figure 4-20 shows the endothermic reactions in blue color and the exothermic reactions in red. In the center of the plasma there was no heat of reactions observed, which was expected since all of the reactants were consumed in the plasma almost immediately. The exothermic reactions occurred mostly at the edge of the plasma, and the endothermic reactions appeared more in the middle of the tube, where the temperature of the gas was higher. The exothermic reactions raised the temperature throughout the tube, however, the endothermic reactions consumed the heat and prevented the temperature from increasing further. Moreover, the gas velocity was the lowest in the center of the tube due to the vortex flow. Therefore, the temperature reduction from the convective heat transfer was minimal in the center of the tube.

The methane, hydrogen and ethyne concentrations are shown in Figure 4-21. These concentrations were used for the calculation of the conversion and the selectivities. The reactions rates were adjusted in a way that the obtained conversion and selectivities were similar to the experimental results. These reaction rate adjustments were universally applied to all of the simulations of the initial methane concentrations that were shown in Figure 4-6.

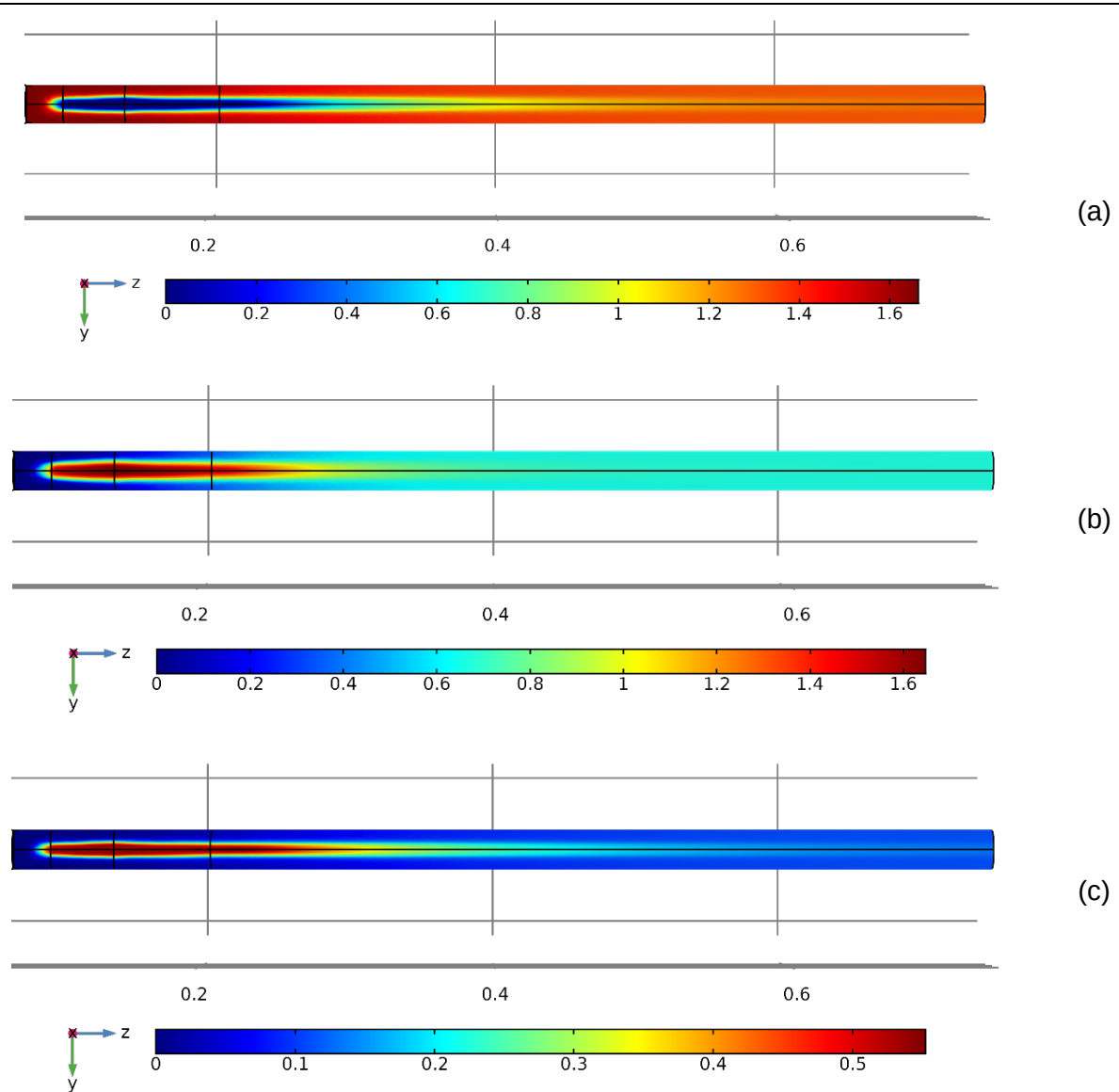


Figure 4-21 (a) CH₄, (b) H₂, (c) C₂H₂ concentration [mol/m³] for 4 vol% CH₄+Ar mix at 70 l/min.

In Figure 4-21 (a) methane was fully consumed in the hottest spot in the plasma and remained unchanged towards the tube outlet, where the gas temperature was not high enough for the commencement of the reactions. Accordingly, hydrogen was generated mostly in the plasma area as shown in Figure 4-21 (b). Similarly, ethyne was also produced mainly in the plasma itself. However, compared to the hydrogen concentration profile in Figure 4-21 (b) the ethyne concentration profile in Figure 4-21 (c) extended further along the length of the outlet tube. This 3D simulation was consistent with the 0D simulation results given in Figure 4-10, where the C₂H₂ production was increased at the longer residence time. The C_xH_y radicals recombined with each other later in the reactor, specifically at the center of the tube, where the reaction times were higher due to the lower gas speed.

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Some ethene was produced as well, which is pictured in Figure 4-22. C_2H_4 was a product of the reaction between the remaining radicals and of the hydrogen together with ethyne.

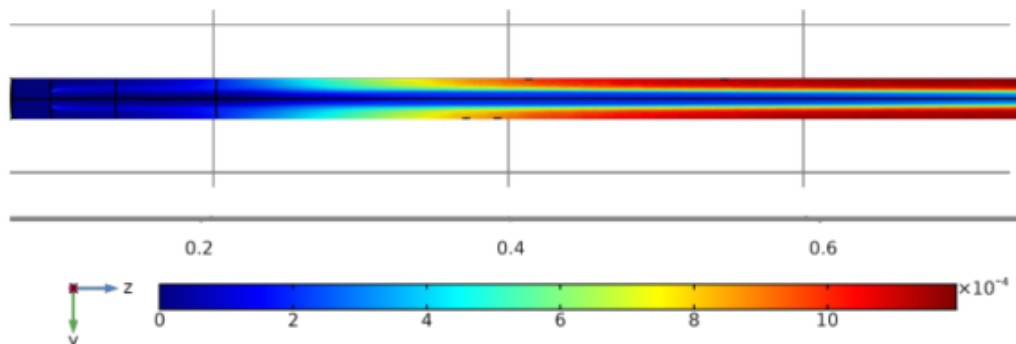


Figure 4-22 C_2H_4 concentration [mol/m³] for 4 vol% CH_4 +Ar mix at 70 l/min.

The ethene concentration magnitude, in Figure 4-22, was 10^{-4} order lower than the hydrogen or ethene concentration, thus, during the experiments only traces of it were detected. Nevertheless, it is worth noting that if the production of ethene is unwanted, then the residence time could be reduced by shortening the outlet tube or by increasing the gas flow rate, for instance.

Figure 9-1 - Figure 9-5 in the Appendix give the closer look at the radicals' formation and consumption rates through the concentration profiles. As previously discussed, the radicals were primarily generated through the dissociation of methane in the plasma region. Additionally, some radicals such as C_2H_3 occurred downstream, along the reactor outlet, resulting from the interactions between methyl radicals and hydrocarbon products.

The comparison between the simulated and the experimental results were summarized in Figure 4-23. The simulated power input was in the range of 500 – 2100 W as in the experiments, and the gas mixture was varied between 4 vol% and 16 vol% CH_4 .

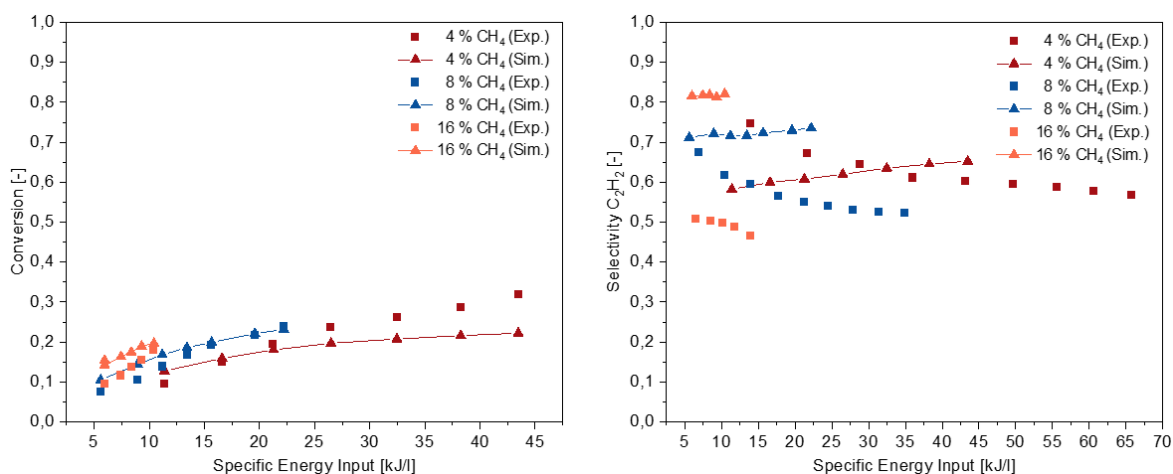


Figure 4-23 Simulated and experimental results with 1 – 16 vol% CH_4 in feed at 70 l/min at varying power supply: CH_4 conversion (left), C_2H_2 selectivity (right).

The simulated methane conversion, which is shown in Figure 4-23, was close to the experimental results. As the power input was increasing - represented in the graph by the Specific Energy Input (SEI) – the methane conversion rose in both the simulated and experimental results. However, the discrepancy between the simulated and experimental results became more pronounced at the higher SEI values. This could be attributed to several factors, for example, the actual shape of the heat source and the temperature levels might differ from the assumptions used in the model. Figure 4-8 illustrated that the plasma shape changed significantly with the increasing power input, indicating that a Gaussian profile was not an ideal representation. Furthermore, the experimental gas temperature shown in Figure 4-6 (a) was derived from an approximation based on the rotational temperature of dicarbon (C_2) molecules and the blackbody radiation measured via the emission spectroscopy [73]. This method introduced the uncertainties of measurement, as it only accounted for the C_2 molecules. Additionally, the accuracy of the spectroscopy was highly dependent on the measurement location, which limited the reliability of the obtained temperature profile.

When the C_2H_2 selectivity was compared between the simulated and experimental results, some discrepancy was also noticeable. Since the initial adjustment of the reaction set was performed for a feed mixture containing 4 vol% CH_4 , the simulation results under these conditions were more accurate. Whereas, for the gas mixture with the most methane content of 16 vol%, the simulated results deviated significantly. The reason was the truncation of the reaction set, and the inherent error of the temperature profile measurement. On the other hand, the simplification of the reaction set was a necessary step, because the computational power was limited. Also, the simulation of carbon as solid was omitted due to its complexity, and some higher hydrocarbons formation was excluded because the experimental gas analyzers were limited to few gas sensors. To obtain a full picture about the reactions set, more rigorous experimental readings would be required, which is cost intensive.

4.6 Summary

To conclude, the methane pyrolysis in the microwave plasma was simulated based on the experimental data. The simulation approach was guided by an analysis of the optical emission spectroscopy and the plasma shape, which was observed through the special windows [73]. The measured gas temperature ranged between 3900 and 4000 K. The plasma shape was approximated by a Gaussian bell curve, with the hottest region located at the center of the plasma torch. The high plasma temperature indicated that the thermal reactions were likely more dominant than the electron impact reactions. Therefore, in the 3D simulation, the plasma was modeled as a heat source. The omission of the electron impact reactions was validated

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using a 0D model, which compared various reaction sets. The most suitable reaction set was identified through this comparison and then applied in the 3D simulation. Out of 274 reactions, 44 thermal reactions were included in the 3D simulation. Moreover, the reaction rates had to be slowed down to help the simulation convergence. If this adjustment was not made, then other solution would be to include very small number of reactions. For instance, in [169] only 4 reactions were included in the model, which was used for the microwave plasma reactor design improvement. In some cases, the chemistry part was excluded from the CFD simulation, where the gas properties were extrapolated from the gas concentrations obtained from the 0D model [170]. The exclusion of the chemical reactions helped the 3D simulation to converge, and the results were used to identify the optimal operating conditions in the microwave plasma for higher gas conversion [170]. There is a clear trade-off between the details incorporated in a simulation and its practical usability. To obtain valuable results - such as enhancing the reactor design and operating conditions within a limited timeframe - simplifying the simulation is essential.

The applied approach confirmed that the assumption of the plasma as a heat source can be made during the atmospheric microwave plasma simulation. Moreover, this method allowed to obtain the 3D simulation where the turbulent gas flow, high gas temperature and the reactions were connected. Thus, the optimal reaction conditions and reactor geometries could be simulated.

5. SDBD reactor

5.1 Introduction

This chapter explains the experimental setup of the SDBD reactor, which was simulated. The SDBD is a non-thermal plasma type, which is different from the thermal plasma GAP and MW discussed in the previous chapters. The simulation of the fluid flow and the chemical reactions were compared with the experimental results to understand the plasma effects. In this early stage, the SDBD reactor was not used for methane pyrolysis. The experiments involved O_2 reactions in the $H_2 + N_2$ mixture. And pure N_2 was used for the flow characterization. Although this reactor was not a part of the methane pyrolysis study, the simulations achieved for the SDBD reactor gave an insight regarding the plasma behavior. The relative simplicity of the reactions between $O_2/N_2/H_2$ species allowed for more rigorous plasma simulation than in the case of CH_4 . The results obtained showed the difference between the non-thermal and thermal plasma simulation approaches. The simulation results complied with the experimental data and are discussed in this chapter.

5.2 Experimental setup

The reactor configuration consisted of the reactor chamber and the SDBD electrode plate where plasma was ignited. The SDBD reactor was positioned inside a gas chamber featuring the narrowed inlet and outlet, as illustrated in Figure 5-1. Internally, the gas chamber was 203 mm long and 105 mm wide and with a height of 16.4 mm. The gas flowed in the horizontal direction along the SDBD plate at 10 l/min flow rate. The feed gas that was used for the reactions contained 500 ppm O_2 , 40 vol% N_2 and 60 vol% H_2 . Chemical reactions were analyzed in terms of O_2 conversion. The gas reactions occurred under atmospheric pressure and ambient temperature conditions. The plasma-induced gas heating resulted in an outlet temperature of approximately 50 °C. As seen in Figure 5-1, the gas chamber had the top and side viewing windows. These were used for the characterization of the plasma glow dimensions and for obtaining the Schlieren images, which were used for the simulation validation.

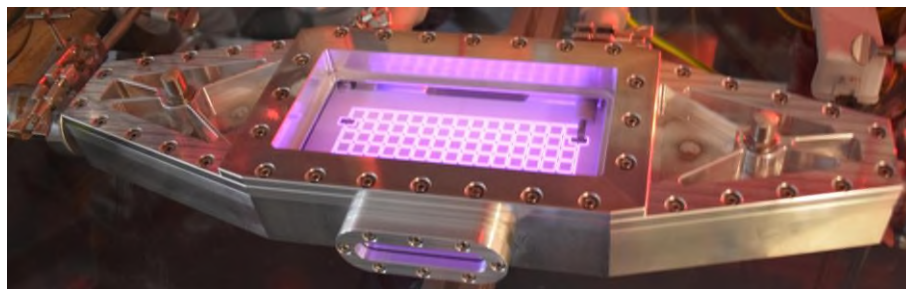


Figure 5-1 Gas chamber with SDBD plasma [171].

5. SDBD reactor

The SDBD plasma presented in Figure 5-1 is shown schematically in greater schematic detail in Figure 5-2. The electrode plate was positioned at the center of the gas chamber, where the SDBD plasma was generated. The electrode consisted of the aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$) dielectric plate and the metal grid structure on both sides. Each grid was 10 mm x 10 mm in size, with the metal coating that was 500 μm wide and 22 μm high. The entire plate, sized at 0.635 mm x 88 mm x 190 mm, accommodated 15 x 5 grids on each side.

The dielectric barrier, in this case the aluminum oxide, played a crucial role in preventing the arc formation by limiting the charge transfer during each discharge event. This led to the charge accumulation on the dielectric surface, which locally modified the electric field and contributed to the self-limiting nature of the discharge [172].

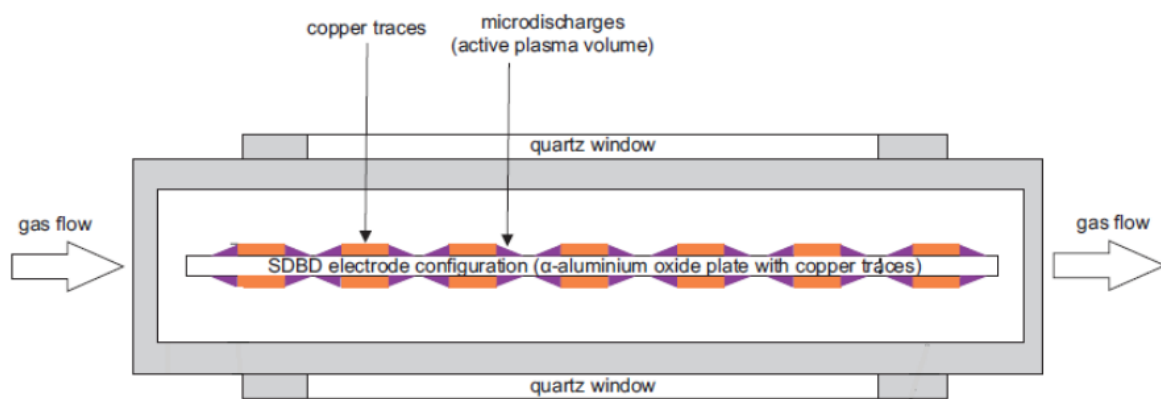


Figure 5-2 SDBD reactor schematic from the side view [173].

The grid and the plate in Figure 5-2 were simulated as the solid domain, and the rest as the fluid.

The grid-shaped electrodes were grounded on one side, while the other side was connected to a high-voltage power generator that supplied a peak-to-peak voltage between 7 kV and 11 kV. The system operated at a pulse frequency of 4000 Hz [173]. The applied power generated numerous transient microdischarges across the dielectric surface. These microdischarges are filamentary in nature and occur within nanoseconds, but due to their high repetition rate and spatial distribution, they collectively formed a quasi-uniform and spatially extended surface discharge [172]. The discharge image is given in Figure 5-1.

The voltage pulses applied to the electrodes are illustrated in the diagram shown in Figure 5-3 [173].

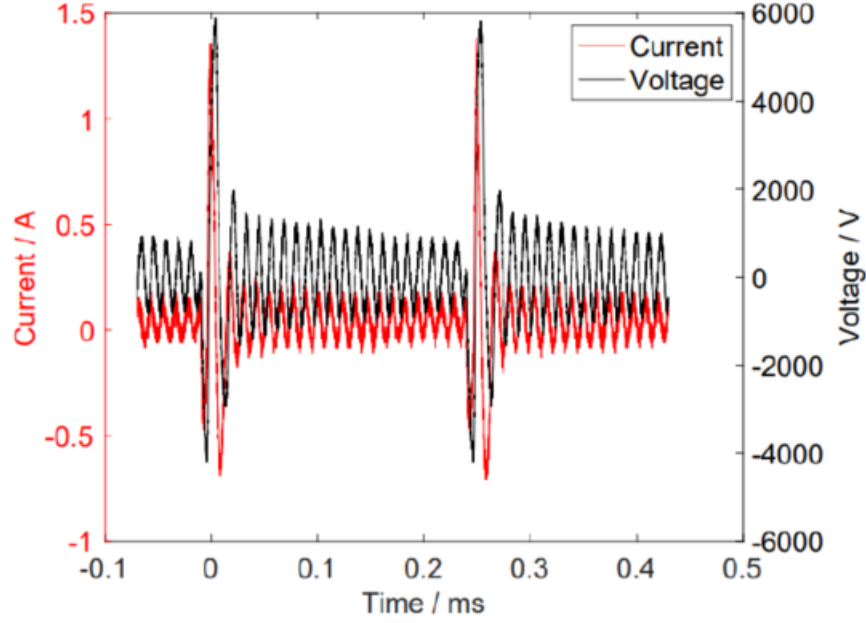


Figure 5-3 Oscillogram measurement of the applied voltage and current [173].

The high voltage peaks in Figure 5-3 represent the plasma ignition. The 4000 Hz frequency of the voltage application was equivalent to the plasma discharge that was sustained for 25 μ s in between the pulses.

In contrast to GAP and MW plasma, the SDBD is a non-thermal plasma. Therefore, the electron impact reactions and interaction of the charged species with the electric field needed to be included in the modeling. The electrons and the ions presented in the plasma were accelerated by the electro hydrodynamic body force, F_{EH} , given in Equation (5-1):

$$F_{EH} = E\rho_f \quad (5-1)$$

where E is the electric field and ρ_f is the charge density.

Since the force exerted by the plasma was in the pulse mode, the electro hydrodynamic body force could be interpreted as:

$$F_{pulse} = \frac{\Delta t}{T_p} F_{EH} \quad (5-2)$$

where Δt is the plasma discharge time, T_p is the pulse interval.

The heat effects from the plasma were approximated by the Joules heating [174]:

$$Q_{Joules} = \vec{e}\mu_e E^2 \quad (5-3)$$

where E is the electric field and μ_e is the electron mobility.

The applied voltage was not constant and pulsated with the peak-to-peak voltage magnitude as shown in Figure 5-3. To compensate for it during the simulation, the root mean square

5. SDBD reactor

voltage was used instead, for instance, the applied voltage of 10 kV was equivalent of 7 kV in the simulation [175].

To capture the plasma effects imposed on the gas flow, the Schlieren images were taken during the experiments. These high-sensitivity optical images visualized the density gradients in the flow field, and allowed the detection of the vortices, and other flow disturbances induced by the SDBD plasma. This method is non-intrusive and offers significant advantages over the particle image velocimetry, which relies on tracers that may be influenced by the plasma and electromagnetic fields [176]. The plasma discharge generated a substantial instantaneous force that propelled the reactive species into the bulk fluid, which led to a fluid-dynamic effect known as the ionic wind [177]. The power supplied for the plasma generation dissipated into the surrounding gas, resulting in heating that altered the gas density. Schlieren imaging effectively captured the density gradients in the flow field and enabled the visualization of the flow behavior induced by the plasma discharge. The resulting Schlieren images were then used to qualitatively and quantitatively validate the simulation results, ensuring that the numerical models accurately represented the plasma and the gas flow interaction dynamics. Figure 5-4 shows the Schlieren image obtained during the experiments. The images were obtained from the side viewing window, and for 2 different feed gases N_2 and H_2 . The dashed lines in Figure 5-4 represent the location of the metal grids with 10 mm x 10 mm dimension, and the middle empty space is the electrode.

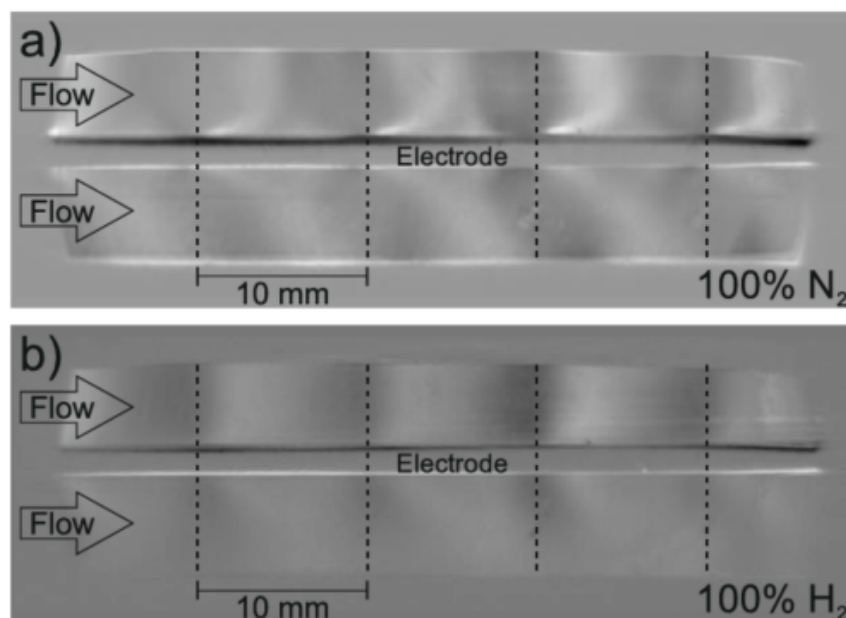


Figure 5-4 Schlieren images for 100 vol% N_2 and 100 vol% H_2 at 10 l/min with active SDBD plasma at 11 kV [178].

The Schlieren images in Figure 5-4 displayed the density variation caused by the plasma. The image intensity was greater for N_2 than H_2 . This was expected, since the nitrogen density

changes more drastically with increasing temperature than the hydrogen density, as shown in Figure 5-5. Therefore, for the simulation gas flow behavior only N_2 was considered and compared with the Schlieren images.

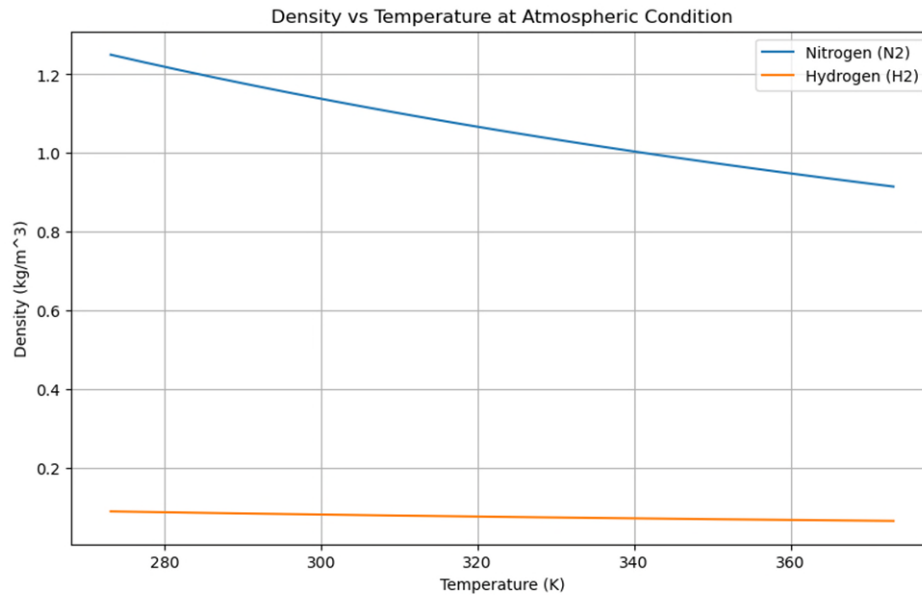


Figure 5-5 Density vs temperature at atmospheric pressure for N_2 and H_2 .

The flow phenomena observed in the Schlieren images were interpreted through the simulation of the gas flow, which incorporated the electro hydrodynamic forces generated by the plasma discharge. The simulations in this work are aimed at explaining how the plasma induced body forces alter the local pressure and velocity fields, leading to the observed density gradients and the flow streamlines. The driving force for the gas conversion in the GAP and MW plasma are the thermal effects from the plasma. In case of the SDBD plasma, the gas temperature stayed almost unchanged, however, the gas conversion was still measured. This proves that the SDBD plasma is a non-thermal plasma, which requires the inclusion of the electron impact reactions to the simulation. Moreover, the volume of the plasma was restricted to the electrode plate and the applied metal grid. Therefore, the simulation of the non-thermal SDBD plasma was more complex, as it required modeling the electron impact reactions and the dynamic interactions between the plasma discharge and the neutral gas in the constrained domain.

5.3 Fluid flow simulation results

As it was mentioned in the previous section, the electrode and dielectric barrier were simulated as a solid domain, whereas the flowing gas was a fluid domain. Initially, the gas flow was simulated without any plasma effects. The obtained velocity profile was then included in the following simulations as the initial condition. The mesh of the gas chamber is given in Figure 5-6 and it contains 2119000 cells. This 3D geometry was utilized for gas flow simulation.

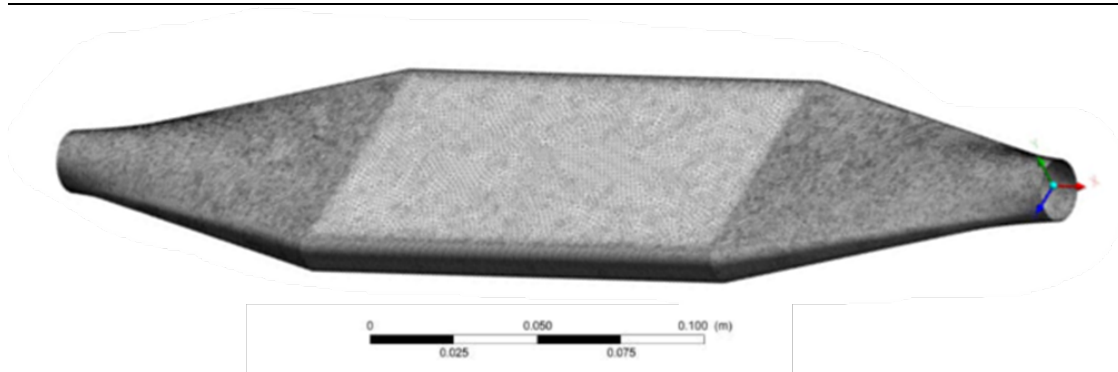


Figure 5-6 Gas chamber mesh.

The 3D model shown in Figure 5-6 was used to evaluate if the laminar flow might be appropriate for the simulation, or if the turbulent flow model was more fitting. According to Equation (2-37), the Reynolds number of N_2 gas at 10 l/min and the atmospheric conditions was 200, which suggested a laminar flow. However, the reactor was narrower at the inlet and the outlet. Therefore, the laminar flow model was compared to the $k-\epsilon$ turbulence model. The vector field of the velocity in the x-direction, parallel to the electrode, is presented in Figure 5-7. The arrow points could indicate if any backflow was occurring. Both the laminar and $k-\epsilon$ model simulations showed similar velocity vector fields. There were no eddies or turbulence formed. This was due to the slim geometry of the electrode plate with $22\text{ }\mu\text{m}$ height and the low gas velocity, which was around 0.1 m/s. The empty channel with protruding squares in Figure 5-7 represents the electrode plate with the metal grid, which is observed from the side view. Moreover, when the streamlines in Figure 5-7 were compared with the Schlieren images in Figure 5-4 a difference between the gas flow characteristics is noticeable. Since the simulation was performed only for the fluid flow without any plasma effects, the gas density was constant. Hence, the bulk magnitude of the gas velocity in Figure 5-7 was homogeneous. This comparison to the experimental data demonstrated that the gas density and consequently velocity were influenced by the plasma discharge.

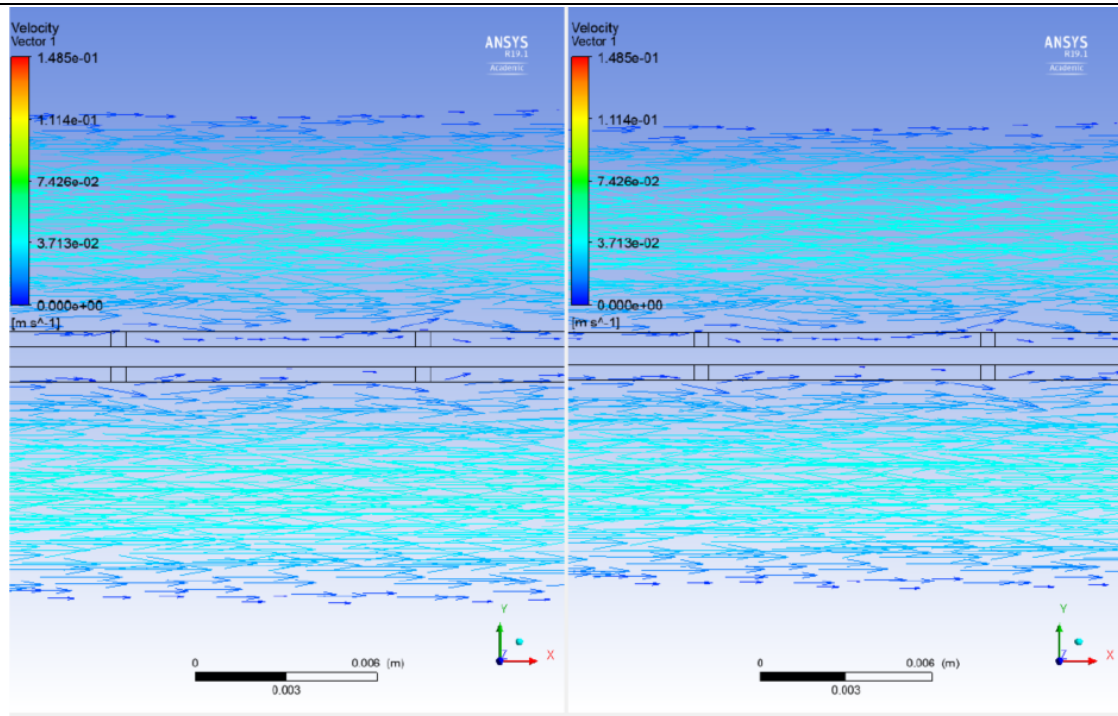


Figure 5-7 Velocity field along the gas flow direction, left: laminar, right: k- ϵ model.

When the velocity magnitude was calculated using the laminar and k- ϵ turbulence model, the values did not differentiate. Figure 5-8 gives the magnitude comparison.

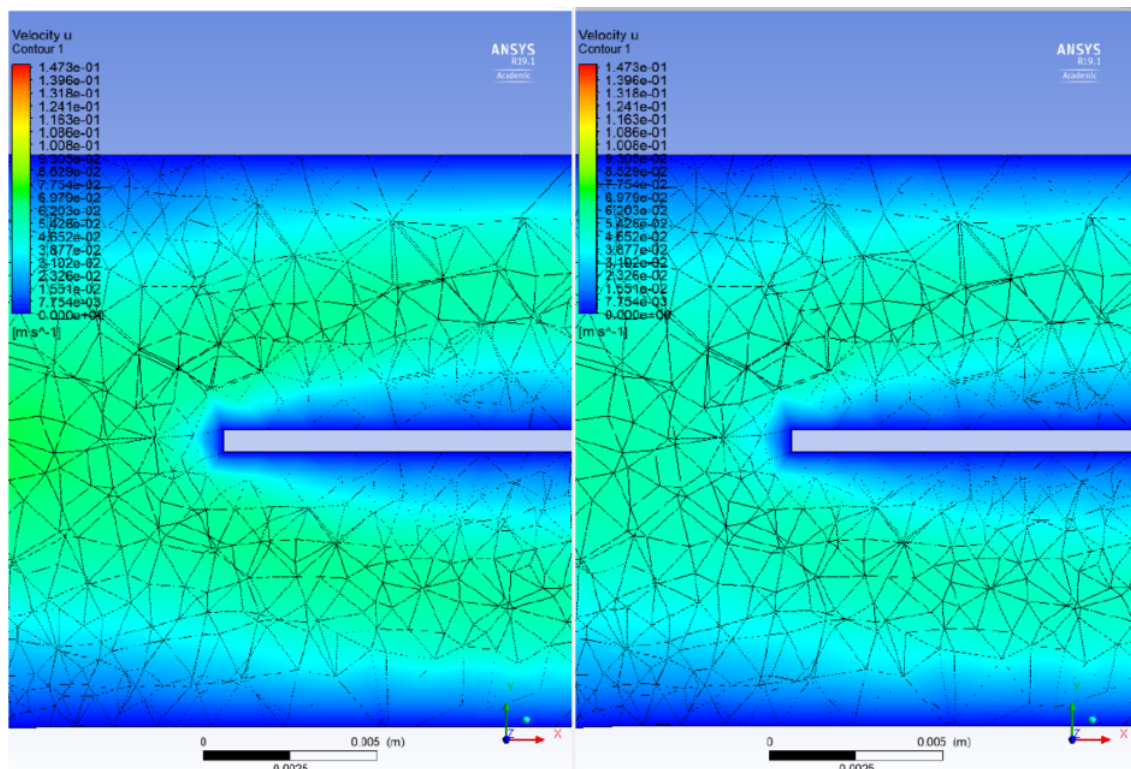


Figure 5-8 Velocity magnitude left: laminar, right: k- ϵ model.

5. SDBD reactor

The 2D side view of the electrode plate in Figure 5-8 shows the gas velocity with lower magnitude on the plate surface, this is explained by the no-slip condition.

To check if the laminar flow exists across the reactor, the 3D geometry was observed from different cut-plane views. As seen in Figure 5-9, five arbitrary planes were selected, where “Plane 3” was located along the center of the reactor, and other 4 were placed symmetrically to either of the sides.

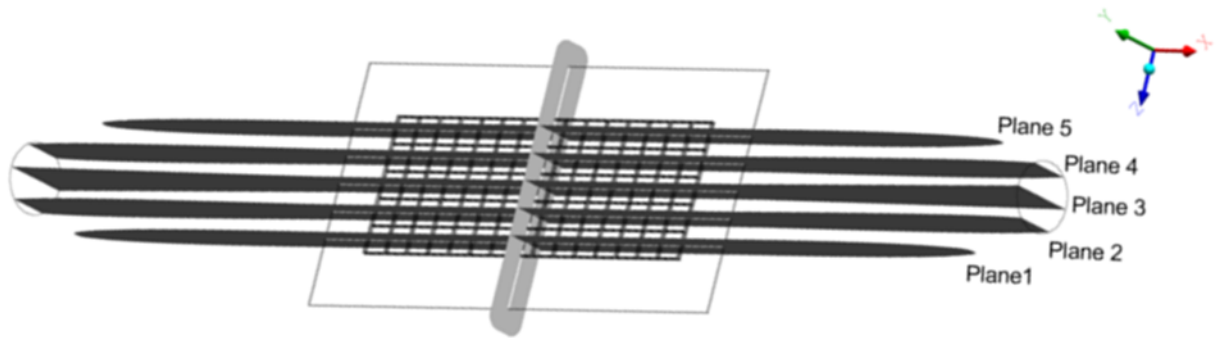


Figure 5-9 Cut-out planes for the flow evaluation.

Figure 5-10 shows the velocity range at the cut-out planes from Figure 5-9. The gas had a homogeneous velocity of 0.1 m/s along the electrode length and width across all cut-out planes. A slighter elevated velocity was calculated at the inlet and outlet of the reactor. The uneven surface of the electrode, formed by the metal grids, did not cause turbulence because the volume of the reactor was significantly larger than the size of the electrode plate.

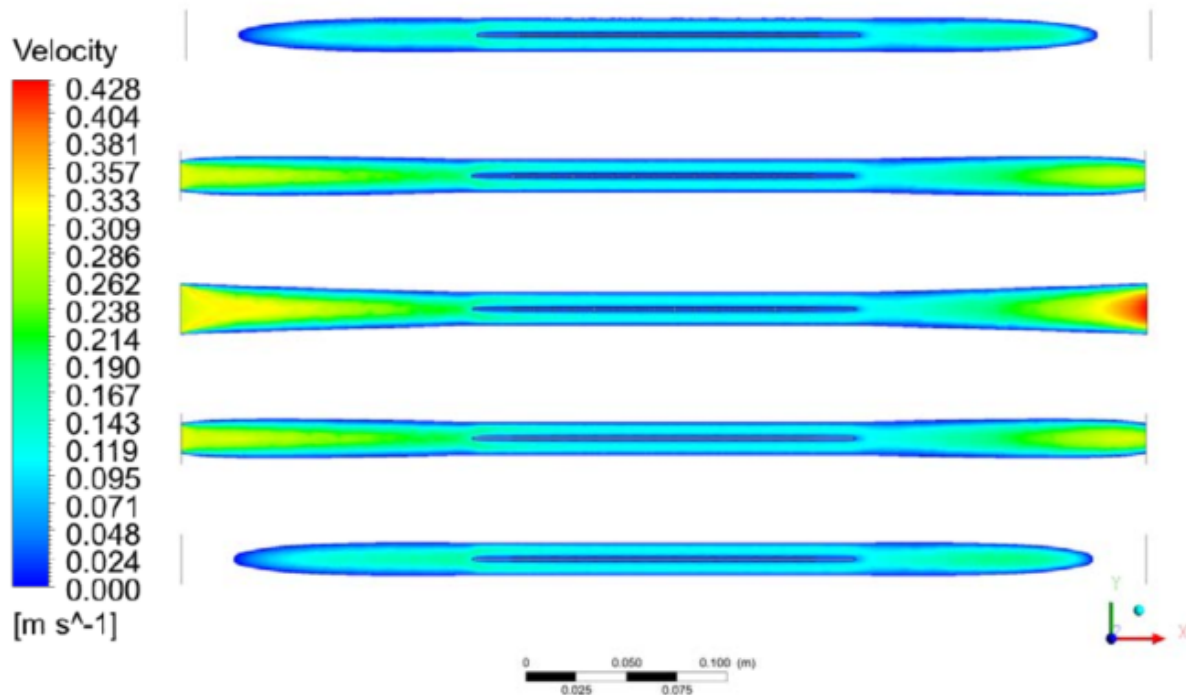


Figure 5-10 Velocity magnitude at different locations across the reactor.

Figure 5-11 presents the velocity profile in the direction normal to the electrode plate, calculated at the middle of the plate. The graph shows that a fully developed flow was present across all locations on the electrode surface, indicating a uniform flow across the whole plate. Therefore, for the following simulation steps, it was sufficient to use a cut plane at the center of the chamber, as this location accurately represented the overall flow behavior.

Furthermore, the velocity profiles in Figure 5-11 above and below the electrode plate are symmetrical. This symmetry was expected, as the electrode plate was positioned centrally within the reactor chamber, equidistant from the both the top and bottom walls. The maximum calculated gas velocity was 0.16 m/s.

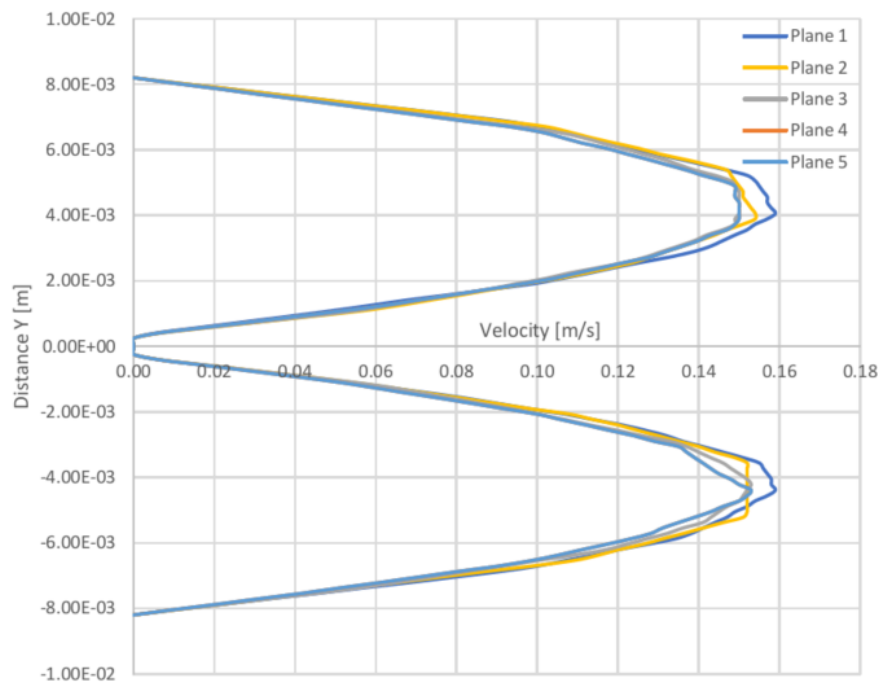


Figure 5-11 Velocity profile comparison across the reactor.

On the other hand, the velocity profile obtained in Figure 5-11 did not resemble the Schlieren image. The Schlieren image presented a clear distinction between the powered and grounded electrode. Thus, the influence of the plasma on the gas flow cannot be ignored, and the flow velocity should be calculated again together with the plasma effects and reactions.

5.4 2D simulation results with plasma discharge effects

This section discusses the results of the 2D simulation of the fluid flow including the influence from the plasma on the flow.

The simulation of the plasma discharge required an extremely fine mesh due to the thin nature of the SDBD plasma layer. As a result, the number of cells needed for a complete 3D simulation would have exceeded the available computational resources. To address this, an

additional 2D geometry was introduced to model the plasma effects. The mesh used in the 2D simulation, shown in Figure 5-12, was already highly refined. Extending this mesh to a 3D domain would have made the simulation computationally unfeasible.

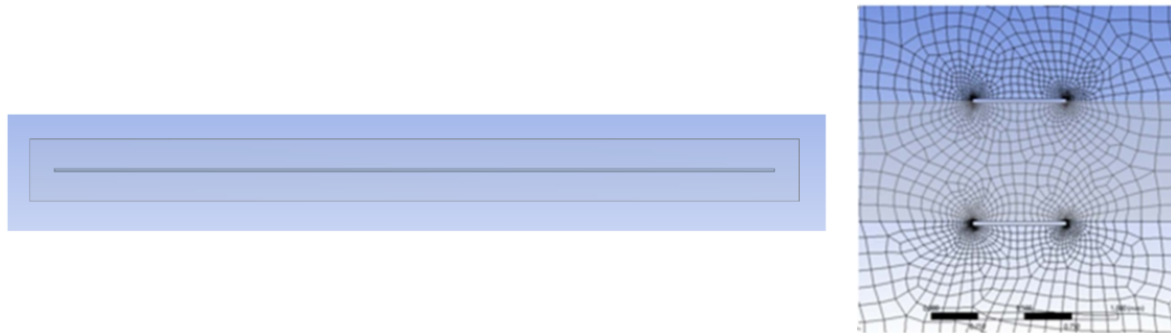


Figure 5-12 2D geometry and the mesh view around the metal grid on the electrode.

The 2D geometry in Figure 5-12 had the same length and height as the gas chamber 203 mm x 16.4 mm. The electrode plate and the metal grid dimensions were as in the experiment. During the simulation, the Al_2O_3 plate and the metal traces were defined as the solid domain, and the rest was specified as the fluid domain. Overall, the mesh shown in Figure 5-12 contained 342400 cells, which is 6 times lower than the 3D geometry mesh. Hence, the plasma discharge effects could be simulated within the acceptable computational time.

Figure 5-13 shows the results of the 2D electric field simulation under a 7 kV voltage, which is equivalent to the 10 kV applied voltage. In this setup, the upper part of the electrode was positively charged, while the lower part was grounded, creating a distinct electric field distribution across the domain.

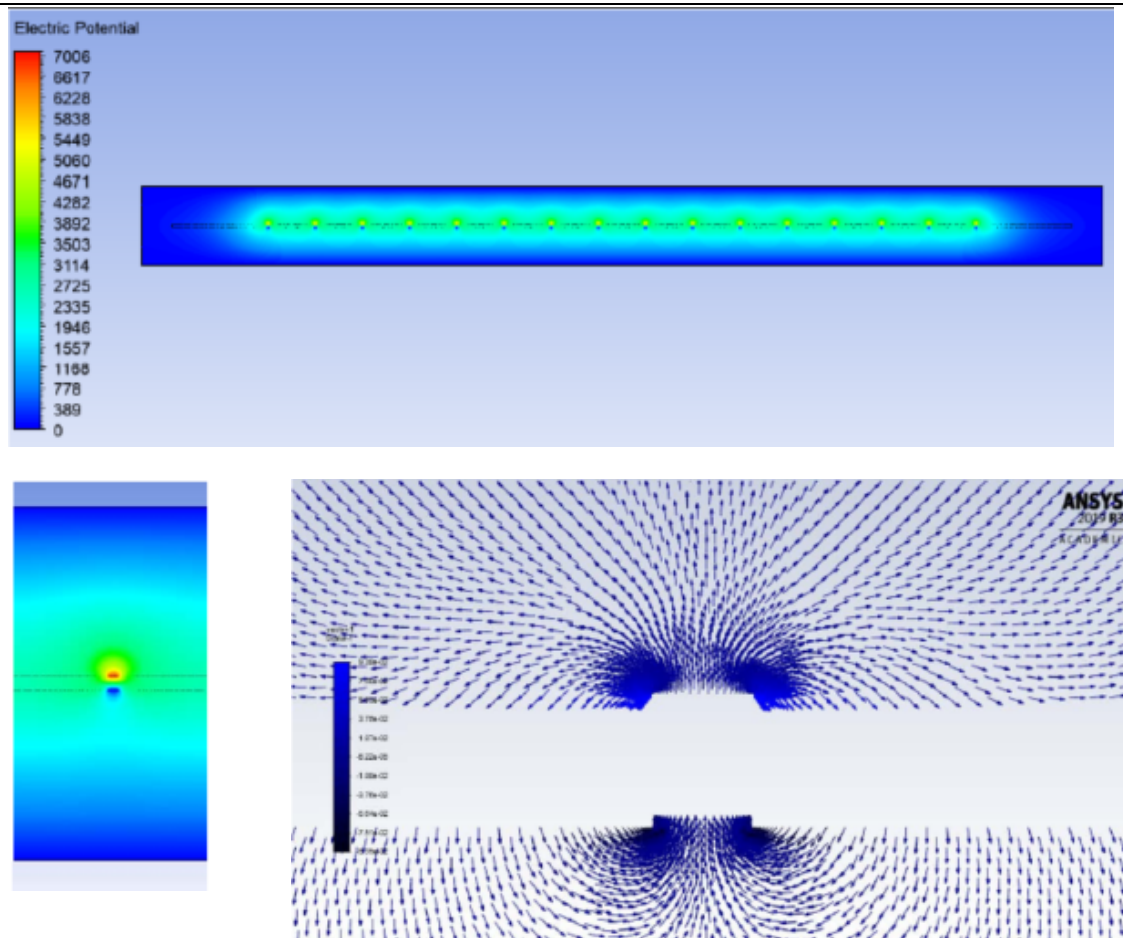


Figure 5-13 Electric potential magnitude and the electric field vectors.

The electric field vectors, as shown in the simulation in Figure 5-13, are pointed from the top part of the electrode toward the bottom, reflecting the applied voltage configuration. The resulting charge density distribution is presented in Figure 5-14, which highlights a representative section of the domain. The charged species were primarily concentrated around the metal traces. When the upper half of the electrode was supplied with the voltage and the lower half was grounded, the positive charges accumulated in the upper region, while the negative charges were concentrated in the lower region. Therefore, the charge density magnitude in Figure 5-14 has a positive sign at the top of the electrode, and the negative one at the bottom.

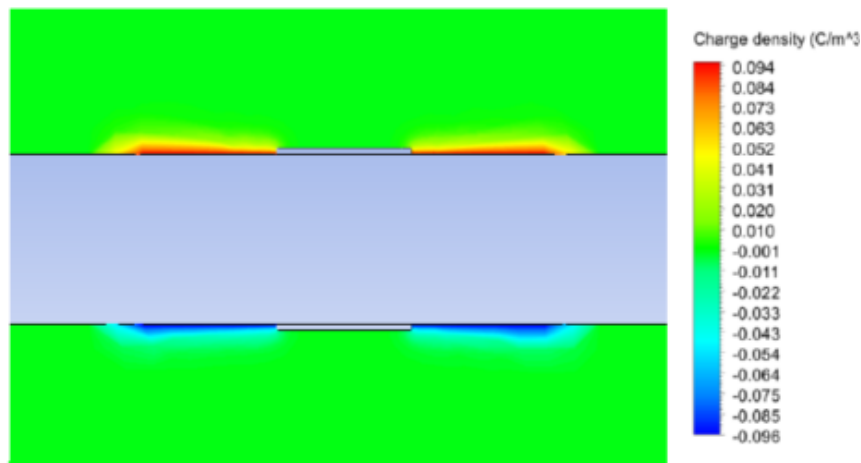


Figure 5-14 Charge density magnitude for one grid element.

The oscillogram in Figure 5-3 showed that the voltage switched between the positive and negative magnitude, hence, the charge polarity on Figure 5-14 changes accordingly depending on the applied voltage.

After the high-voltage electric field ionized the gas near the electrode and created the charged particles, the electro hydrodynamic forces induced by the plasma would accelerate the charged particles in the gas and transfer the momentum to the neutral molecules. As a result, Figure 5-15 shows the 2D gas velocity profile, which has been influenced by the plasma discharge.

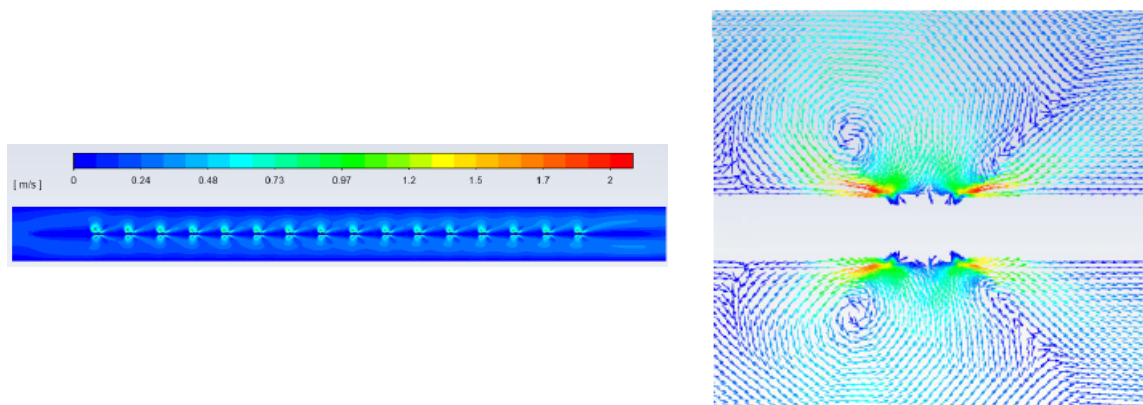


Figure 5-15 Velocity profile influenced by the plasma discharge effects and the close-up of the vector field around one grid element.

The velocity profile in Figure 5-15 differs from the laminar flow in Figure 5-7. Note that the turbulence k - ω -SST model was used to simulate the gas flow influenced by the plasma discharge effects. In this context, the plasma species were accelerated by the ionic wind - a phenomenon driven by the electro hydrodynamic interactions. These interactions occur when charged particles in the plasma exert forces on the surrounding neutral molecules, resulting

in a net flow of gas. The momentum transfer from the ions to the neutral molecules generated a directed flow [179].

As shown in Figure 5-15, the gas velocity was highest near the plasma region. This is because the ions produced by the plasma discharge were accelerated by an electric field. Therefore, the regions of the strong electric field and high gas velocity coincide spatially. Once the gas was accelerated by the charged species, the turbulence was developed, leading to the vortex formation.

The plasma already contains the reactive species that facilitate the conversion of the gas into the desired product. The additional formation of the vortices enhanced the interaction between the neutral gas and plasma, thereby improving the overall gas conversion rate [178].

The ionic wind strength was proportional to the charge density and the electric field strength, thus, the increase in the voltage supply raised the gas acceleration effect from electro hydrodynamic force. Figure 5-16 shows the achieved velocity magnitude at the different applied voltages at 0.1 mm distance along the electrode plate. The y-axis in Figure 5-16 is the space between the electrode surface and the gas chamber, which is 8.2 mm.

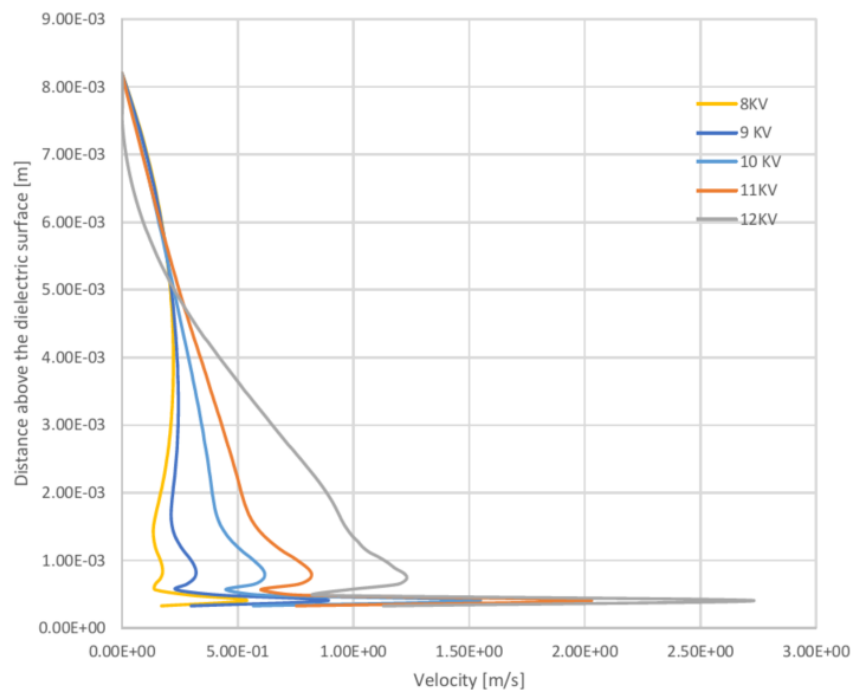


Figure 5-16 Velocity magnitude from electrode plate till gas chamber top wall for varying applied voltage.

The velocity at the gas chamber wall was zero according to the no-slip condition. The highest gas velocity was observed in the vicinity of the plasma, which was ranged between 0.5 – 2.7 m/s depending on the applied voltage. This confirms the influence of the plasma on the gas behavior, because in Figure 5-11 only 0.16 m/s gas velocity was reached, where no

5. SDBD reactor

plasma effects were considered. Approximately 0.5 mm above the electrode plate, the velocity magnitude decreased for all applied voltages, which was attributed to the vortex formation induced by the ionic wind.

The heat generated by the SDBD plasma was modeled using the Joules heating approximation [174]. The resulting temperature profile, corresponding to a flow rate of 10 l/min of pure nitrogen gas and the applied voltage of 10 kV, is shown in Figure 5-17. The gas entered the mixing chamber at the ambient conditions, approximately 300 K, and exited the chamber at around 400 K.

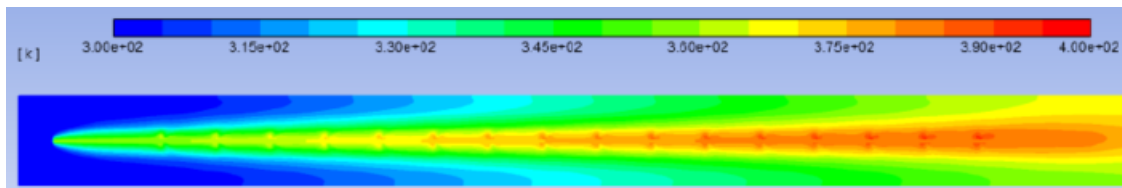


Figure 5-17 Temperature profile for 10 l/min N₂ at 10 kV.

The experimental results indicated a temperature increase of approximately 50 K, reaching around 323 K [178]. In contrast, the simulation predicted a temperature rise of about 100 K. This discrepancy was primarily due to the adiabatic boundary conditions assumed in the simulation, which neglected the heat losses to the environment. In reality, the thermal energy dissipates to the surroundings, resulting in a lower observed temperature increase.

To compare the Schlieren images with the simulation results, the nitrogen density profile obtained from the simulation was analyzed. As shown in Figure 5-18, the simulated density profile closely resembled the experimental Schlieren image. The lower density regions were observed near the electrode, where higher temperatures occurred due to the plasma activity. Additionally, the repetitive pattern introduced by the metal grid in the simulation mimicked the visual features seen in the experimental setup.

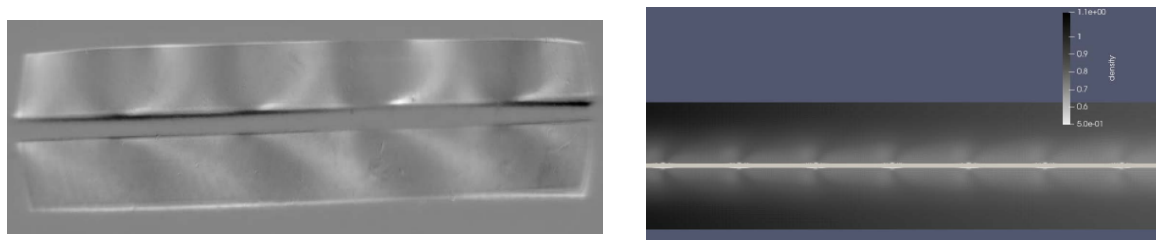


Figure 5-18 Schlieren image (left) vs N₂ density profile at 10 l/min.

However, a discrepancy between the experimental and simulation results was observed. In the Schlieren image, the density gradient extended to the top and bottom boundaries of the gas chamber. In contrast, the simulation showed the density gradient dissipating near the chamber walls, where it remained relatively constant. This difference can be attributed to the

use of a two-dimensional geometry in the simulation, which was chosen due to the computational limitations. As a result, the plasma effects such as ionic wind and the heat transfer across the width of the electrode plate were not captured. This loss of the dimensional detail contributed to the inconsistency with the experimental observations. Nevertheless, the simulation successfully captured the overall impact of the plasma discharge on the gas flow behavior and characteristics.

5.5 SDBD plasma chemistry simulation

To incorporate SDBD reactions into the previously performed fluid flow simulation, beforehand, the 0D simulation was conducted. The resulting gas composition from this 0D simulation was then used to upgrade the 2D simulation.

The 0D simulation was performed using a feed gas mixture of 500 ppm O_2 , 40 vol% N_2 , and 60 vol% H_2 with an applied power of 35 W, as measured during the experiment. The simulation duration was set to 250 μs , corresponding to the peak-to-peak duration of the plasma discharge shown in Figure 5-3. The results, presented in Figure 5-19, show a minor conversion of O_2 and a rapid formation of the reactive radicals such as O, OH, and HO_2 , along with the conversion product H_2O .

Although a significant amount of O and H radicals was generated during the 250 μs discharge, the consumption of O_2 and H_2 was not visibly changed in the temporal mole fraction profiles. This is because the concentrations of O_2 and H_2 were much higher than those of the formed radicals and products, resulting in a nearly flat mole fraction and number density profiles for O_2 and H_2 in Figure 5-19.

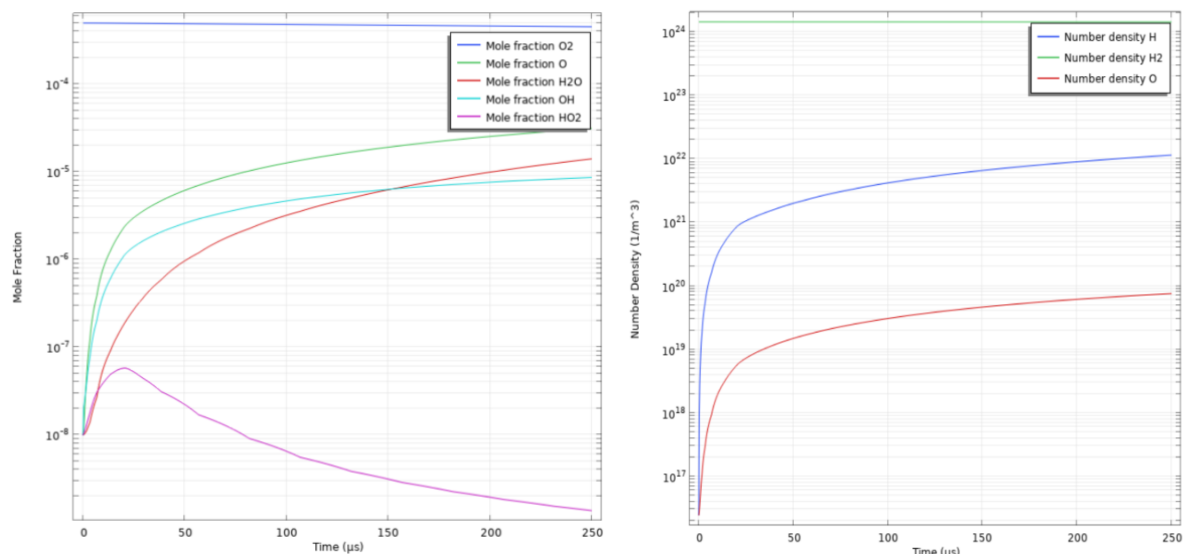


Figure 5-19 Mole fraction of O_2 and H_2 consumption and radicals O and H formation.

5. SDBD reactor

A significant discrepancy existed between the oxygen conversion observed in the 0D simulation and the experimental results. While nearly 100% O_2 conversion was achieved during the SDBD plasma experiments [178], the 0D simulation showed only minor conversion. This difference may be attributed to simplifications in the reactor geometry and the exclusion of the electro hydrodynamic forces that influence the gas conversion. Additionally, the 0D simulation covered only a single discharge event lasting 250 μs , which is much shorter than the actual residence time of 2.1 ms.

Due the computational constraints, it was not achievable to simulate the full 2.1 ms duration with a detailed reaction set comprising 135 reactions, including the electron impact reactions. Therefore, for the subsequent 2D simulation, where the gas flow behavior was combined with the reactions' kinetics, the reaction mechanism was simplified to ensure the computational feasibility.

For the 2D simulation, the Miller mechanism for $O_2 + H_2$ chemistry was employed [103]. This mechanism included 20 reactions involving the neutral species such as O_2 , H_2 , OH , O , H , HO_2 and H_2O . The initial gas composition was derived from the 0D simulation results, ensuring that the plasma discharge effect on the reaction activation was incorporated into the model. Additionally, the initial velocity vector field was taken from the gas flow simulation under the plasma discharge effects, as shown in Figure 5-15. The graphical representation of the 2D simulation approach is given in Figure 5-20.

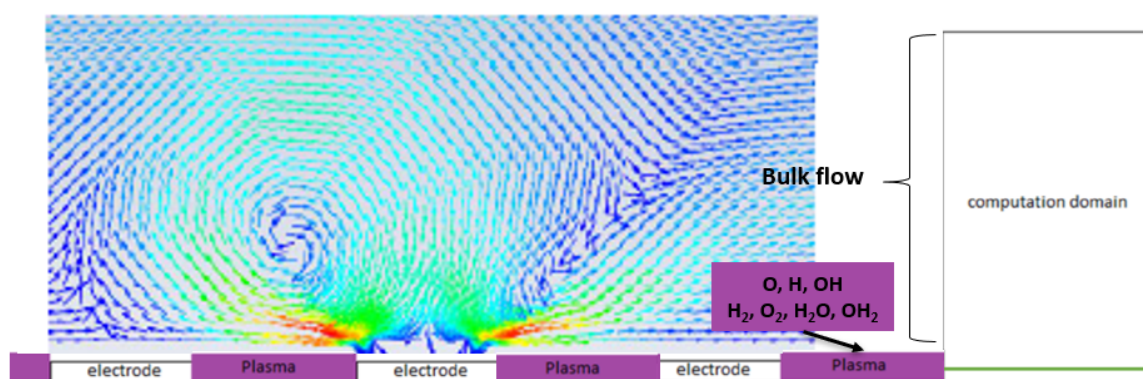


Figure 5-20 The computational domain for one plasma cell simulation.

As previously discussed, the steep concentration gradients of the reactive species, combined with the vortex flow and the thin geometry of the electrode, make the simulation computationally intensive. To model the combined effects of the SDBD plasma, including the gas acceleration due to the ionic wind, together with the chemical reactions and heat and mass transfer between the plasma and bulk flow, a representative computational domain was defined, as shown in Figure 5-20.

This domain was restricted to a rectangular area measuring 5 mm in width and 8.2 mm in height. It represents half the distance between the adjacent metal grids, where the plasma from one grid connects with the plasma from the neighboring grid. This setup aligned with the SDBD plasma image presented in the Appendix (Figure 9-6). The simulation results discussed below correspond to a single discharge event.

From the reaction kinetics it is known that the immediate conversion product of O_2 is the O radical. The concentration profile of O in Figure 5-21 shows that the most active region for the O_2 conversion was directly at the electrode.

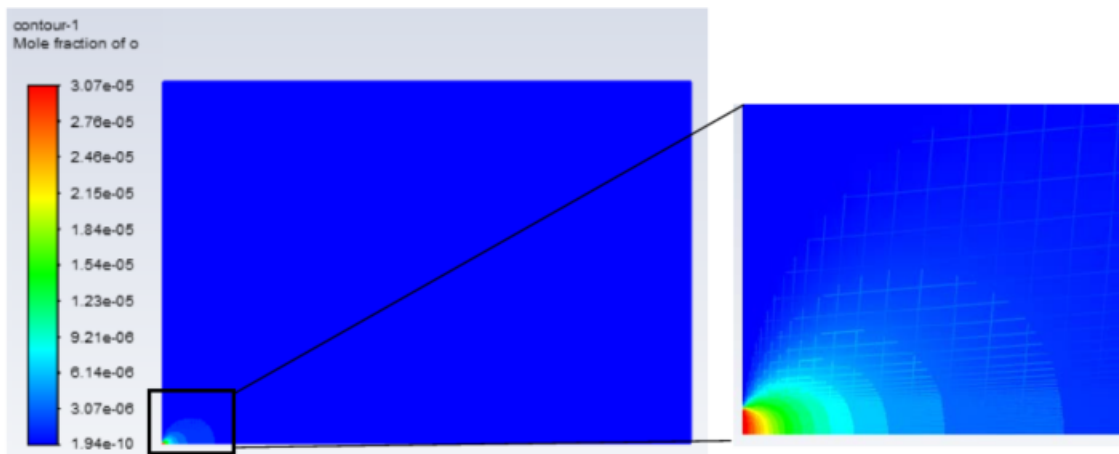


Figure 5-21 O radical mole fraction, where $n_0(O) = 3.1 \cdot 10^{-5} \text{ mol/mol}$.

The oxygen concentration profile shown in Figure 5-22 indicated that the reaction activity was the highest near the plasma source. This suggests that plasma-induced processes significantly enhance O_2 conversion in the immediate vicinity of the discharge region.

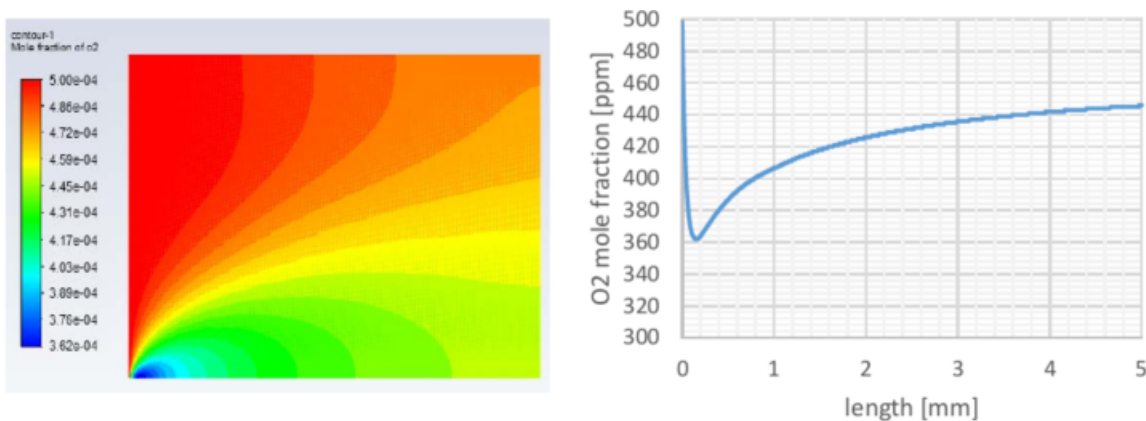


Figure 5-22 O_2 mole fraction, where $n_0(O_2) = 5 \cdot 10^{-4} \text{ mol/mol}$.

The plasma discharge at one electrode grid showed that O_2 concentration decreased from 500 ppm to 440 ppm, which was equal to 12 % conversion. The extrapolated conversion across all 15 grid segments, as shown in Figure 5-23, yielded an overall oxygen conversion

rate of approximately 84 %. This result closely aligned with the experimental measurements, confirming the validity of the simulation approach.

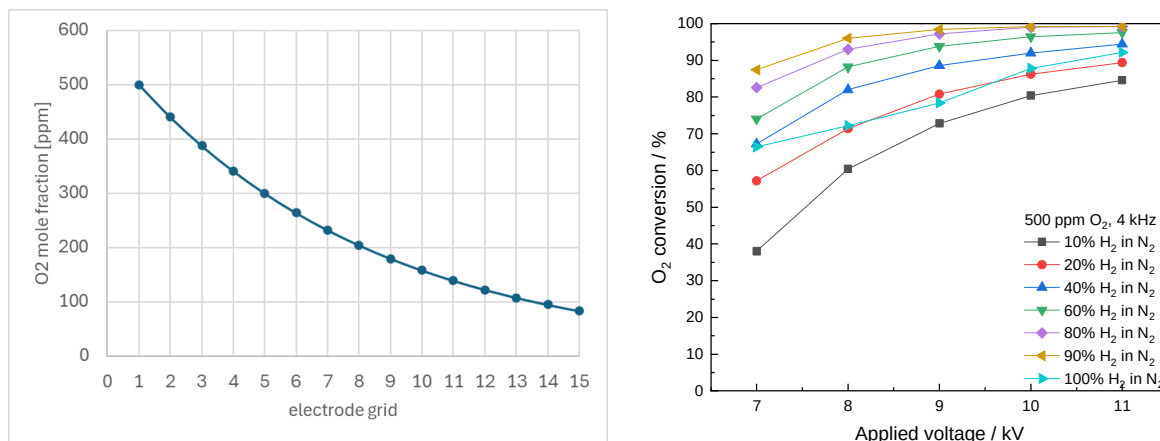


Figure 5-23 The comparison between the O₂ conversion from the simulation (left) vs the experimental results (right).

In the future simulations, the number of modeled metal grid segments could be increased to better reflect the actual experimental setup and improve the accuracy of the results.

5.6 Summary

Overall, the simulation produced reliable and consistent results, demonstrating that the key physical and chemical effects included in the model significantly contributed to the oxygen conversion. The use of a detailed flow model, rather than a simplified laminar flow assumption, proved essential, as it captured important phenomena such as the gas acceleration and backward eddying induced by the ionic wind. Neglecting these effects would have led to an underestimation of the influence of the plasma discharge on the flow dynamics.

Furthermore, incorporating the Joules heating into the simulation allowed for the evaluation of the thermal effects generated by the SDBD plasma, which are critical for understanding the temperature dependent reaction kinetics.

The simplification of the reaction mechanism, along with the use of 0D simulation results in the 2D simulation, effectively reduced the computational costs while still capturing the essential plasma-chemical interactions. This approach enabled the simulation to converge while maintaining the physical relevance.

Importantly, this simulation framework provides a solid foundation for the future studies. It can be extended and adapted to investigate more complex systems, such as the methane pyrolysis in the SDBD plasma, offering valuable insights into the reaction mechanisms, energy efficiency, and reactor optimization.

6. Simulation Software comparison

6.1 Introduction

For this work a combination of various software was utilized, to obtain the simulation results comparative to the experimental outcomes in a limited time. All of the simulations shown here follow the bottom-up methodology, for the sequential modeling of the plasma reactor, transitioning from 0D to 3D [17]. The software employed include COMSOL Multiphysics™, Ansys Fluent®, and OpenFOAM®. To provide an outlook for future work in this field, an overall comparison of these packages based on the experience acquired is presented in this work.

6.2 COMSOL Multiphysics™

COMSOL Multiphysics™ is a sophisticated software platform utilized for simulating and modeling various physical phenomena through the finite element analysis across the multiple disciplines. Comparing it to the other fluid dynamics simulation software used in this work, the advantage of COMSOL Multiphysics™ is its user-friendly interface that enabled to intuitively construct the model by layering the governing equations one-by-one. This flexibility allowed for the straightforward integration of the various physics, including fluid dynamics, heat transfer, electromagnetism, and chemical reactions, thereby facilitating a comprehensive simulation [180].

While COMSOL Multiphysics™ offers powerful tools for simulating the multiphysics systems, it has several limitations when applied to the plasma research. These limitations can affect the accuracy of the results, reduce the computational efficiency, and restrict the feasibility of simulating the complex plasma environments. COMSOL Multiphysics™ rely on predefined models and assumptions, which may not accurately capture the underlying physics of the plasma systems. The complexities of the real plasma behaviors, which can be unpredictable, may necessitate more sophisticated modeling approaches that extend beyond what COMSOL Multiphysics™ natively supports [180]. Moreover, the computational efficiency of COMSOL Multiphysics™ is often questioned when dealing with the large-scale plasma simulations. The finite element method simulations can be computationally intensive, particularly when simulating the complex geometries and multiphysics phenomena of plasma. Such computational expenses can result in longer processing times and may limit the scope of the simulations that can be conducted [181].

For the 0D modeling and simulations, COMSOL Multiphysics™ provided an effective array of built-in functions that allowed for a quicker assessment of the plasma chemistry. However, during the 2D simulations, COMSOL Multiphysics™ faced convergence challenges and

required careful tuning of the simulation parameters. In contrast, OpenFOAM® offered greater flexibility and speed in obtaining the simulation results due to its inherent characteristics.

6.3 OpenFOAM®

OpenFOAM® is an open-source computational fluid dynamics toolbox that provides a robust framework for tackling the problems involving the turbulent flows, magnetohydrodynamics, and plasma simulations due to its flexibility and extensive capabilities in modeling the complex physical phenomena [182]. OpenFOAM® supports the multiphysics simulations, allowing to couple the different physical models of the fluid dynamics and plasma simulation with the external solvers. This highlights the essential interactions without requiring the multiple software environments [183]. The software is designed for the high-performance computing and can efficiently utilize the parallel computing resources. This is especially advantageous for the simulations that demand the substantial computational power, such as those used to model the intricate dynamics within the plasma reactors [184].

However, there are several disadvantages of OpenFOAM® software. The learning curve associated with OpenFOAM® can be steep, due to its less user-friendly interface based on the C++ programming language. Although, OpenFOAM® offers the considerable flexibility, it does not have the built-in plasma physics models as COMSOL Multiphysics™. The models needed to be developed from the basic principles of the plasma, which was time-consuming and required a strong understanding of the underlying physics [182].

6.4 ANSYS Fluent®

Another CFD software is ANSYS Fluent®, which is one of the leading CFD software widely utilized for simulating the fluid flow, heat transfer, and chemical reactions across the various engineering applications. Similarly to COMSOL Multiphysics™, ANSYS Fluent® features a graphical user interface that simplifies the model setup, running the simulations, and visualizing the results. This ease of use enhances the modeling iterations and accelerates the workflow for the simulations [185]. Moreover, the software has a solid reputation for the accuracy due to extensive validation against the experimental data and established benchmarks, instilling reliability of the simulation results [186].

Although user-friendly, the advanced customization, especially for the unique plasma models and boundary conditions, required the considerable expertise while using ANSYS Fluent®. The simulations involving the complex geometries or transient phenomena demanded the substantial computational power and time, and led to the convergency problems.

ANSYS Fluent® was suitable for the 2D simulations but necessitated the modifications to address the specific challenges. In terms of 3D modeling, both ANSYS Fluent® and

OpenFOAM® facilitated faster simulations, whereas COMSOL Multiphysics™ struggled with the convergence issues even after simplifying the plasma model.

6.5 Summary

By strategically combining these software tools and leveraging their individual strengths, valuable insights into the plasma reactors could be obtained within a relatively short timeframe. Ensuring the integration across the clearly defined boundaries enhanced the overall efficiency and accuracy of the simulations. Table 6-1 summarizes the application of COMSOL Multiphysics™, ANSYS Fluent®, and OpenFOAM® in this context.

Table 6-1 Software application at various levels [17].

Software	0D	2D	3D	Application summary
COMSOL Multiphysics™	+	±	-	Reaction set refinement
ANSYS Fluent®	-	+(with modification)	+	Fluid flow and heat transfer effects
OpenFOAM®	-	+	+	Fluid flow, heat transfer and plasma interactions

“+” and “-” indicate the applicability of the software for the various modelling levels.

7. Conclusion

In conclusion, the methane pyrolysis plasma simulations were performed for the gliding arc plasma reactor and the microwave plasma. The surface dielectric barrier discharge plasma was simulated for $O_2/H_2/N_2$ mixture, with the potential application in methane pyrolysis. For the achievement of the simulation results in the limited time and manageable computational effort, a combination of the CFD software, namely COMSOL Multiphysics™, ANSYS Fluent® and OpenFOAM® was applied. This allowed for the compensation of the drawbacks and limitations of each software, while still obtaining the consistent results comparative to the experimental findings. The experiments were performed in the Ruhr University Bochum, and the collaboration was a part of the “Me²H₂ project” for the methane pyrolysis funded by Federal Ministry of Education and Research (FKZ 03SF0571A-G).

During the gliding arc plasma reactor simulation, various reactor geometries were tested to improve the arc stability and methane conversion. The initial plasma characterization used nitrogen, later switching to methane and argon mixture, which simplified the plasma ignition. Therefore, the simulations were performed with different gas mixtures as in the experiments. A bottom-up approach was applied to achieve the simulation: the reaction set was reduced with the 0D simulation results, and the 2D simulations modeled the gliding arc behavior, including the discharge effects and the electron impact reactions. Insights from the 2D model were then extended to the 3D simulations.

This simulation strategy significantly reduced the computational effort, even when integrating the turbulent flow and the complex reaction sets. The reactor geometry improvements were identified in the 3D simulations, including increasing the inlet diameters from 1 mm to 2 mm to stabilize the arc and extend the residence time. Additionally, adjusting the cathode cap improved the methane conversion from 35 % to 44 %.

The key finding of the simulations is that the methane pyrolysis in the GAP reactor is primarily thermally driven, meaning the plasma arc can effectively serve as a simplified heat source. Furthermore, such assumptions allowed to simulate the improvements to the reactor geometry, which were validated by the experiments.

The stepwise simulation approach 0D → 2D → 3D was applied to model the microwave plasma reactor. The 0D simulation helped to identify a suitable methane-argon reaction set. The analysis showed that, similarly to the GAP reactor, the reactions in MW plasma are thermally driven as well. Therefore, the plasma was modeled as a heat source. The optical emission spectroscopy helped to model the plasma shape and approximated the heat source with the Gaussian profile.

As a result, during the 3D simulation, the influence of the high plasma temperatures on the gas flow behavior, and on the methane conversion was considered. The simulation results were validated by the hydrogen and ethyne selectivities, as well as the methane conversion, which were obtained from the experiments at the varying gas compositions and applied power. The simulation outcomes closely matched the experimental data and can be used to optimize the methane conversion and hydrogen selectivity by adjusting the operating conditions and reactor design. For instance, the highest methane conversion was measured for the most diluted methane content, which was 64.5 % conversion for the 1 vol% CH₄ in the feed gas at 60 l/min flow rate [38]. On the other hand, the hydrogen selectivity was the lowest for the 1 vol% CH₄ mixture. Therefore, the simulations could help to identify the optimal feed content and the gas flow rate and reduce the number of the experiments. The outlined approach could be used to simulate different reactor geometries as for the GAP reactor. The concentration profiles of the reactive radicals obtained from the simulations could be used as the guide for the possible reactor geometries, such as the additional quenching and different inlet nozzles configurations [163] [181].

An additional simulation was conducted for the surface dielectric barrier discharge plasma reactor, focusing on a different reaction set than the methane pyrolysis. For the SDBD simulation, a simpler gas mixture of O₂/H₂/N₂ was used. Moreover, compared to the gliding arc or microwave plasma, the SDBD plasma simulation domain was smaller, as it was formed on the surface of the electrode plate and was confined by a metal grid. This allowed for a more detailed plasma simulation.

In this case, the electromagnetic effects of the plasma discharge on the gas flow were successfully simulated and compared with Schlieren imaging. Unlike the GAP and MW plasmas, SDBD is the non-thermal plasma. Therefore, it could not be simplified as a thermal plasma. While the thermal plasmas relied on the high gas temperatures to drive the reactions, the SDBD plasma operated near the ambient temperatures, and the gas conversion was primarily driven by the electron impact.

The simulation also revealed the formation of the ionic wind - an effect visible in the Schlieren images. The velocity profiles obtained for the simulation of the gas flow without and with the plasma discharge effects, revealed that the ionic wind could accelerate the gas from 0.16 m/s to 2.7 m/s gas velocity. Moreover, the backflow mixing was discovered with the simulation, which explained the high gas conversion rate, even at a relatively low gas temperature [172].

These findings demonstrated that the model can be extended to test other gas mixtures and reactor configurations in the future, such as the stacking of the electrodes to enhance the conversion efficiency.

7. Conclusion

The work showed that the plasma simulation is not a trivial task, which requires a fundamental understanding of the ongoing physical and electro-magnetic phenomena. The modeling software is limited and cannot provide a ready-to-use package. However, the combination of the available commercial and open-source software made it possible to build the simulation of the plasma in a systematic way. This approach gave the freedom of modeling and was not restricted only for one type of the plasma reactor, and on the other hand, the same strategy was used to simulate the thermal and non-thermal plasmas. The obtained simulation results were used for the reactor geometry optimization, with the measured positive results in terms of the methane conversion. For example the conversion improvement in the GAP reactor from 35% to 44 % by the reactor modifications suggested from the simulation results [38] [81].

The findings presented in this work contribute to a deeper understanding of methane pyrolysis in plasma. One of the primary challenges in this field is enhancing the overall energy efficiency of the process, to make it more economically attractive. The problematic can be effectively addressed through the strategic reactor design optimization and the selection of the operating parameters. In this context, the computational fluid dynamics simulations serve as a powerful tool, enabling the detailed analysis of the plasma behavior, heat transfer, and flow dynamics, thereby guiding the development of more efficient and scalable reactor configurations.

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9. Appendix

For Equation (2-9) $C(f(\varepsilon))$ – collision terms for the following collision types: electron-neutral elastic collision, where only kinetic energy is exchanged (9-1); electron-neutral inelastic collision that involves excitation of the neutral particle (9-2); electron-neutral superelastic collision, where electrons gain energy (9-3), electron-electron collision, where the energy transferred between through the electron density (9-4), are calculated as follows [82]:

$$C(f(\varepsilon)) = \frac{d}{d\varepsilon} \left[\frac{2m_e}{M} \varepsilon^2 \sigma_{el}(\varepsilon) \left(f(\varepsilon) + k_B T_g \frac{df(\varepsilon)}{d\varepsilon} \right) \right] \quad (9-1)$$

$$C(f(\varepsilon)) = \sum_{i,j} \delta_i [(\varepsilon + \varepsilon_{ij}) \sigma_{ij}(\varepsilon + \varepsilon_{ij}) f(\varepsilon + \varepsilon_{ij}) - \varepsilon \sigma_{ij}(\varepsilon) f(\varepsilon)] \quad (9-2)$$

$$C(f(\varepsilon)) = \sum_{j,i} \delta_j [(\varepsilon - \varepsilon_{ij}) \sigma_{ij}(\varepsilon - \varepsilon_{ij}) f(\varepsilon - \varepsilon_{ij}) - \varepsilon \sigma_{ji}(\varepsilon) f(\varepsilon)] \quad (9-3)$$

$$C(f(\varepsilon)) = \frac{d}{d\varepsilon} \left[8\pi \left[\frac{\tilde{e}^2}{4\pi\varepsilon_0 m_e} \right]^2 \ln \frac{12\pi n_e \lambda_D^3}{v_e^3 n_e} \varepsilon^{\frac{3}{2}} \left(I(\varepsilon) f(\varepsilon) + J(\varepsilon) \frac{df(\varepsilon)}{d\varepsilon} \right) \right] \quad (9-4)$$

where i, j – states of the species, σ – cross sectional data, λ_D – Debye length, $I(\varepsilon)$ and $J(\varepsilon)$ – Spitzer integrals, v_e – momentum transfer frequency.

Table 9-1 Chemical kinetic reactions of neutral species for pure methane [160].

No.	Reaction	Forward rate coefficient		
		A (cm ³ mol ⁻¹ s ⁻¹)	n	E (kJ mol ⁻¹)
1	CH ₄ + H → CH ₃ + H ₂	2.2E+4	3	36.75
2	CH ₃ + H → CH ₂ + H ₂	1.8E+12	0	63.2
3	CH ₂ + H → CH + H ₂	3.00E+13	0	0
4	CH ₂ + H ₂ → CH ₃ + H	7.23E+13	0	0
5	CH ₃ + H ₂ → CH ₄ + H	4.13E+04	2.5	39.4
6	H ₂ + H + H → H ₂ + H ₂	9.70E+16	-0.6	0
7	CH ₃ + CH ₂ → C ₂ H ₄ + H	5.00E+13	0	0
8	CH ₃ + CH ₃ → C ₂ H ₅ + H	5.00E+12	0.1	44.4
9	CH ₃ + CH ₃ → C ₂ H ₅ + H	5.62E+00	0.08	45.2
10	C ₂ H ₅ + H → C ₂ H ₄ + H ₂	1.30E+37	-8.15	184.3
11	C ₂ H ₅ → C ₂ H ₄ + H	1.25E+38	-8.2	189.4
12	C ₂ H ₄ + H → C ₂ H ₃ + H ₂	3.16E+11	0.7	33.5
13	C ₂ H ₄ + CH ₃ → C ₂ H ₃ + CH ₄	4.20E+11	0	46.5
14	C ₂ H ₄ + H ₂ → C ₂ H ₂ + H ₂ + H ₂	7.54E+17	0	332
15	C ₂ H ₄ + H ₂ → C ₂ H ₃ + H ₂ + H	7.54E+17	0	404.0

16	$\text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_2 + \text{H}$	3.00E+13	0	0
17	$\text{C}_2\text{H}_2 + \text{H} \rightarrow \text{C}_2\text{H}_3$	1.13E+36	-7.65	35.5
18	$\text{CH}_2 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	1.80E+13	0	0
19	$\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	8E+12	0	11
20	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}$	6.21E+11	0	14
21	$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	1.31E+34	-6.34	455.2
22	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2$	1.70E+09	0.56	52.6
23	$\text{CH} + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_2 + \text{H}$	1.1E+13	0	0
24	$\text{C}_3\text{H}_2 + \text{H} \rightarrow \text{C}_3\text{H}_3$	6E+12	0	0
25	$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_2 + \text{H} + \text{H}_2$	2.9E+5	0	0
26	$\text{CH} + \text{H} \rightarrow \text{C} + \text{H}_2$	1.50E+14	0	0
27	$\text{CH}_3 + \text{C} \rightarrow \text{C}_2\text{H}_2 + \text{H}$	5.00E+13	0	0
28	$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$	4.13E+2	2.5	39.4

Table 9-2 Electron impact reactions for pure methane [48].

No.	Reaction	Collision type	Energy loss (eV)
29	$\text{e} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} + \text{e}$	Attachment	-
30	$\text{e} + \text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2 + \text{e}$	Attachment	-
31	$\text{e} + \text{CH}_4 \rightarrow \text{e} + \text{CH}_4\text{s}$	Elastic	-
32	$\text{e} + \text{CH}_4 \rightarrow \text{e} + \text{e} + \text{CH}_4^+$	Ionization	12.6
33	$\text{e} + \text{CH}_4 \rightarrow \text{e} + \text{e} + \text{H} + \text{CH}_3$	Ionization	14.3
34	$\text{e} + \text{H}_2 \rightarrow \text{e} + \text{e} + \text{H}_2^+$	Ionization	15.4
35	$\text{e} + \text{CH}_2 \rightarrow \text{e} + \text{e} + \text{CH}_2^+$	Ionization	11
36	$\text{e} + \text{CH} \rightarrow \text{e} + \text{e} + \text{CH}^+$	Ionization	11

Table 9-3 Surface reactions for pure methane with reaction rate dependent on sticking coefficient (equal to 1) and diffusive length $\frac{1}{\Lambda^2} = \left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{R}\right)^2$, where L and R are arc length and radius [188].

No.	Reaction
37	$\text{CH}_4^+ \rightarrow \text{CH}_4$
38	$\text{CH}_3^+ \rightarrow \text{CH}_3$
39	$\text{CH}_2^+ \rightarrow \text{CH}_2$
40	$\text{CH}^+ \rightarrow \text{CH}$
41	$\text{H}_2^+ \rightarrow \text{H}_2$

42	$C_2H_2^+ \rightarrow C_2H_2$
43	$C_2H_4^+ \rightarrow C_2H_4$

Table 9-4 Reactions for 0D modeling of argon-methane mixture.

No.	Reaction	Reaction rate
1	$e+CH_4 \rightarrow e+CH_4$	[83] [189]
2	$e+H_2 \rightarrow e+H_2$	[83] [189]
3	$e+CH_2 \rightarrow e+CH_2$	[83] [189]
4	$e+CH_3 \rightarrow e+CH_3$	[83] [189]
5	$e+C_2H_2 \rightarrow e+C_2H_2$	[83] [189]
6	$e+C_2H_4 \rightarrow e+C_2H_4$	[83] [189]
7	$e+Ar \rightarrow e+Ar$	[83]
8	$e+Ar \rightarrow e+Ar_s$	[83]
9	$e+Ar_s \rightarrow e+Ar$	[83]
10	$e+Ar \rightarrow 2e+Ar^+$	[83]
11	$e+Ar_s \rightarrow 2e+Ar^+$	[83]
12	$Ar^++e+e \rightarrow Ar + e$	[83]
13	$e+CH_3^+ \rightarrow C+H_2+H$	[96] [190]
14	$e+CH_2^+ \rightarrow C+H_2$	[96] [190]
15	$e+CH_2^+ \rightarrow C+2H$	[96] [190]
16	$H+CH_4 \rightarrow CH_3+H_2$	[191]
17	$H+CH_3 \rightarrow CH_2+H_2$	[191]
18	$H+C_2H_6 \rightarrow C_2H_5+H_2$	[191]
19	$H+C_2H_5 \rightarrow 2CH_3$	[191]
20	$H+C_2H_5 \rightarrow C_2H_4+H_2$	[191]
21	$H+C_2H_4 \rightarrow C_2H_3 + H_2$	[191]
22	$CH_3 + CH_3 \rightarrow C_2H_6$	[191]
23	$CH_3 + CH_3 \rightarrow C_2H_5 + H$	[191]
24	$CH_3 + CH_3 \rightarrow C_2H_4 + H_2$	[191]
25	$CH_3 + CH_2 \rightarrow C_2H_4 + H$	[191]
26	$CH_3^++CH_4 \rightarrow CH_4^++CH_3$	[191]
27	$Ar^++CH_4 \rightarrow Ar+H+CH_3^+$	[192]
28	$Ar^+ + C_2H_2 \rightarrow Ar + C_2H_2^+$	[193]
29	$C_2H_2^++CH_4 \rightarrow C_2H_3^++CH_3$	[96]

30	$C_2H_4^+ + C_2H_3 \rightarrow C_2H_3^+ + C_2H_4$	[96]
31	$C_2H_4^+ + H \rightarrow C_2H_3^+ + H_2$	[96]
32	$C_2H_3^+ + H \rightarrow C_2H_2^+ + H_2$	[96]
33	$C^+ + CH_4 \rightarrow C_2H_2^+ + H_2$	[96]
34	$C^+ + CH_3 \rightarrow C_2H^+ + H_2$	[96]
35	$C_2H^+ + CH_4 \rightarrow C_2H_2^+ + CH_3$	[96]
36	$H_2^+ + CH_4 \rightarrow CH_4^+ + H_2$	[96]
37	$H_2^+ + CH_4 \rightarrow CH_3^+ + H_2 + H$	[96]
38	$H^+ + CH_4 \rightarrow CH_4^+ + H$	[96]
39	$H^+ + CH_4 \rightarrow CH_3^+ + H_2$	[96]
40	$CH_4 + CH_3 \rightarrow H + C_2H_6$	[96]
41	$CH_4 \rightarrow CH_3 + H$	[96]
42	$CH_3 + C_2H_4 \rightarrow C_2H_3 + CH_4$	[96]
43	$CH_3 + C_2H_3 \rightarrow C_2H_2 + CH_4$	[96]
44	$CH_3 + H_2 \rightarrow CH_4 + H$	[96]
45	$CH_3 + H \rightarrow CH_4$	[96]
46	$H_2^+ + C_2H_2 \rightarrow H_2 + C_2H_2^+$	[96]
47	$H_2 + C_2H_2^+ \rightarrow H + C_2H_3^+$	[96]
48	$C_2H_3 + C_2H_2^+ \rightarrow C_2H_2 + C_2H_3^+$	[96]
49	$C_2H_3 + C_2H_3^+ \rightarrow C_2H + C_2H_5^+$	[96]
50	$C_2H_4 + C_2H_3^+ \rightarrow C_2H_2 + C_2H_5^+$	[96]
51	$C_2H^+ + CH_2 \rightarrow CH_3^+ + C_2$	[96]
52	$C_2H + H \rightarrow H_2 + C_2$	[96]
53	$2C_2H_5 \rightarrow C_2H_3^+ + C_2H_4$	[96]
54	$C_2H_5 + C_2H_3 \rightarrow 2C_2H_4$	[96]
55	$C_2H + C_2H_3 \rightarrow 2C_2H_2$	[96]
56	$C_2H_4 + H_2 \rightarrow C_2H_6$	[96]
57	$C_2 + H_2 \rightarrow C_2H + H$	[96]
58	$C_2 + Ar^+ \rightarrow 2C + Ar^+$	[96]
59	$Ar + Ar + Ar \rightarrow Ar + Ar + Ar$	[83]

Table 9-5 Reactions between excited nitrogen and neutral species [92].

No.	Reaction	Forward rate coefficient		
		A (cm ³ mol ⁻¹ s ⁻¹)	n	E (kJ mol ⁻¹)
1	CH ₄ + N ₂ [*] → CH ₃ + H + N ₂	1.5E-12	0	0
2	CH ₃ + N ₂ [*] → CH ₂ + H + N ₂	4.5E-11	0	0
3	CH ₂ + N ₂ [*] → CH + H + N ₂	3.8E-11	0	0
4	CH + N ₂ [*] → CH + H + N ₂	1.5E-12	0	0
5	C ₂ H ₆ + N ₂ [*] → C ₂ H ₅ + H + N ₂	3.6E-12	0	0
6	CH ₄ + N [*] → CH ₃ + NH	1.5E-12	0	0

Table 9-6 Reactions between neutral species for nitrogen-methane mixture [92].

No.	Reaction	Forward rate coefficient		
		A (cm ³ mol ⁻¹ s ⁻¹)	n	E (kJ mol ⁻¹)
7	CH ₄ + CH ₃ → C ₂ H ₅ + H ₂	1.7E-11	0	11500
8	CH ₄ + CH ₂ → CH ₃ + CH ₃	7.1E-12	0	5020
9	CH ₄ + CH → C ₂ H ₄ + H	5.0E-11	0	200
10	CH ₄ + C ₂ H ₃ → C ₂ H ₄ + CH ₃	2.4E-24	4.0	2754
11	CH ₄ + C ₂ H → C ₂ H ₂ + CH ₃	3.0E-12	0	250
12	CH ₄ + H → CH ₃ + H ₂	2.2E-20	3.0	4045
13	CH ₃ + CH ₃ → C ₂ H ₆	4.0E-10	-0.4	0
14	CH ₃ + CH ₂ → C ₂ H ₄ + H	7.0E-11	0	0
15	CH ₃ + CH → C ₂ H ₃ + H	5.0E-11	0	0
16	CH ₃ + C → C ₂ H ₂ + H	8.3E-11	0	0
17	CH ₃ + C ₂ H ₅ → C ₂ H ₄ + CH ₄	1.9E-12	0	0
18	CH ₃ + C ₂ H ₅ → C ₃ H ₈	4.7E-11	0	0
19	CH ₃ + C ₂ H ₃ → C ₂ H ₂ + CH ₄	6.5E-13	0	0
20	CH ₂ + CH ₂ → C ₂ H ₄	1.7E-12	0	0
21	CH ₂ + CH ₂ → C ₂ H ₂ + H ₂	1.8E-10	0	400
22	CH ₂ + CH ₂ → C ₂ H ₂ + 2H	2.0E-11	0	400
23	CH ₂ + CH → C ₂ H ₂ + H	6.6E-11	0	0
24	CH ₂ + C → C ₂ H + H	8.3E-11	0	0
25	CH ₂ + C ₂ H ₃ → C ₂ H ₂ + CH ₃	3.0E-11	0	0
26	CH ₂ + C ₂ H → C ₂ H ₂ + CH	3.0E-11	0	0
27	CH + CH → C ₂ H ₂	2.0E-10	0	0
28	C ₂ H ₅ + C ₂ H ₅ → C ₂ H ₆ + C ₂ H ₄	2.4E-12	0	0
29	C ₂ H ₅ + C ₂ H ₅ → C ₄ H ₁₀	1.9E-11	0	0
30	C ₂ H ₅ + C ₂ H ₃ → C ₂ H ₆ + C ₂ H ₂	8.0E-13	0	0
31	C ₂ H ₅ + C ₂ H ₃ → C ₂ H ₄ + C ₂ H ₄	8.0E-13	0	0
32	C ₂ H ₅ + C ₂ H → C ₂ H ₂ + C ₂ H ₄	3.0E-12	0	0
33	C ₂ H ₅ + H → C ₂ H ₆	6.0E-11	0	0
34	C ₂ H ₅ + H → CH ₃ + CH ₃	6.0E-11	0	0
35	C ₂ H ₅ + H → C ₂ H ₄ + CH ₃	3.0E-12	0	0
36	C ₂ H ₃ + H → C ₂ H ₂ + H ₂	2.0E-11	0	0
37	C ₂ H ₆ + CH ₃ → C ₂ H ₅ + CH ₄	2.5E-31	6.0	3043

38	$\text{C}_2\text{H}_6 + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_2$	6.0E-12	0	0
39	$\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$	2.4E-15	1.5	3730
40	$\text{C}_2\text{H}_2 + \text{H} \rightarrow \text{C}_2\text{H} + \text{H}_2$	1.0E-10	0	14700
41	$\text{CH}_3 + \text{N} \rightarrow \text{HCN} + \text{H}_2$	1.4E-11	0	0
42	$\text{CH}_3 + \text{N} \rightarrow \text{H}_2\text{CN} + \text{H}$	1.3E-10	0	0
43	$\text{CH}_2 + \text{N} \rightarrow \text{HCN} + \text{H}$	8.3E-11	0	0
44	$\text{CH}_2 + \text{N} \rightarrow \text{CN} + \text{H}_2$	1.6E-11	0	0
45	$\text{CH} + \text{N} \rightarrow \text{CN} + \text{H}$	2.1E-11	0	0
46	$\text{H}_2\text{CN} + \text{N} \rightarrow \text{HCN} + \text{NH}$	6.7E-11	0	0
47	$\text{CN} + \text{N} \rightarrow \text{C} + \text{N}_2$	3.0E-10	0	0
48	$\text{CH}_4 + \text{CN} \rightarrow \text{HCN} + \text{CH}_3$	7.0E-13	2.3	-16
49	$\text{CH}_3 + \text{H} + \text{N}_2 \rightarrow \text{CH}_4 + \text{N}_2$	6.0E-29	-1.8	0
50	$\text{C}_2\text{H}_2 + \text{H} + \text{N}_2 \rightarrow \text{C}_2\text{H}_3 + \text{N}_2$	1.05E-7	-7.27	3632
51	$\text{H} + \text{H} + \text{N}_2 \rightarrow \text{H}_2 + \text{N}_2$	1.5E-29	-1.3	0
52	$\text{N} + \text{N} + \text{N}_2 \rightarrow 2\text{N}_2$	8.3E-34	0	500

Table 9-7 Surface reactions for nitrogen-methane mixture [92].

No.	Reaction	Forward rate coefficient		
		A ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	n	E (kJ mol^{-1})
53	$2\text{H} + \text{wall} \rightarrow \text{H}_2$	9.2E2	0.5	4930
54	$2\text{N} + \text{wall} \rightarrow \text{N}_2$	2.5	0.5	1680

Table 9-8 Reactions between neutral species for H₂ + O₂ gas mixture [101].

No.	Reaction	Forward rate coefficient		
		A ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	n	E (cal mol^{-1})
1	$\text{H}_2 + \text{O}_2 \rightarrow 2\text{OH}$	1.70E+13	0	47780
2	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	1.17E+9	1.3	3626
3	$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	4.00E+14	-0.5	0
4	$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	5.06E+4	2.67	6290
5	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	3.61E+17	-0.72	0
6	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	7.5E+12	0	0
7	$\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$	1.4E+14	0	1073
8	$\text{O} + \text{HO}_2 \rightarrow \text{O}_2 + \text{OH}$	1.4E+13	0	1073
9	$2\text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	6.0E+8	1.3	0
10	$2\text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	1.0E+18	-1	0
11	$2\text{H} + \text{H}_2 \rightarrow 2\text{H}_2$	9.2E+16	-0.6	0
12	$2\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}$	6.0E+19	-1.25	0
13	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	1.6E+22	-2	0
14	$\text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M}$	6.2E+16	-0.6	0
15	$2\text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	1.89E+13	0	-1788
16	$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	1.25E+13	0	0
17	$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2.0E+12	0	0
18	$\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$	1.3E+17	0	45500
19	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{HO}_2 + \text{H}_2$	1.6E+12	0	3800
20	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	1.0E+13	0	1800

Table 9-9 Electron impact reactions of H₂/O₂/H₂O for SDBD plasma.

No.	Reaction	Type of Reaction	Reaction rate
1	$e + O \rightarrow O^+ + 2e$	Ionization	[103]
2	$e + O_2 \rightarrow O^+ + O + 2e$	Ionization	[103]
3	$e + O_2 \rightarrow O_2^+ + 2e$	Ionization	[103]
4	$e + H \rightarrow H^+ + 2e$	Ionization	[103]
5	$e + H_2 \rightarrow H^+ + H + 2e$	Ionization	[103]
6	$e + H_2 \rightarrow H_2^+ + 2e$	Ionization	[103]
7	$e + OH \rightarrow OH^+ + 2e$	Ionization	[103]
8	$e + H_2O \rightarrow H_2O^+ + 2e$	Ionization	[103]
9	$e + H_2O \rightarrow OH^+ + H + 2e$	Ionization	[103]
10	$e + H_2O \rightarrow H^+ + OH + 2e$	Ionization	[103]
11	$e + H_2O \rightarrow O^+ + H_2 + 2e$	Ionization	[103]
12	$e + O_2(a) \rightarrow O_2^+ + 2e$	Ionization	[103]
13	$e + H_2 \rightarrow 2H + e$	Dissociation	[103]
14	$e + O_2 \rightarrow 2O + e$	Dissociation	[103]
15	$e + O_2 \rightarrow O + O^1D + e$	Dissociation	[103]
16	$e + OH \rightarrow O + H + e$	Dissociation	[103]
17	$e + H_2O \rightarrow OH + H + e$	Dissociation	[103]
18	$e + H_2O \rightarrow O^1D + H_2 + e$	Dissociation	[103]
10	$e + O_2(a) \rightarrow 2O + e$	Dissociation	[103]
20	$H_2^+ + e \rightarrow H + H$	Neutralization	[103]
21	$H_3^+ + e \rightarrow 3H$	Neutralization	[103]
22	$H_3^+ + e \rightarrow H_2 + H$	Neutralization	[103]
23	$O_2^+ + e \rightarrow O + O$	Neutralization	[103]
24	$O_2^+ + e \rightarrow O + O^1D$	Neutralization	[103]
25	$O_2^+ + e \rightarrow O^1D + O^1D$	Neutralization	[103]
26	$OH^+ + e \rightarrow O + H$	Neutralization	[103]
27	$H_2O^+ + e \rightarrow OH + H$	Neutralization	[103]
28	$H_2O^+ + e \rightarrow O + H_2$	Neutralization	[103]
29	$H_2O^+ + e \rightarrow O + H + H$	Neutralization	[103]
30	$H_3O^+ + e \rightarrow OH + H + H$	Neutralization	[103]
31	$H_3O^+ + e \rightarrow O + H_2 + H$	Neutralization	[103]
32	$H_3O^+ + e \rightarrow OH + H_2$	Neutralization	[103]
33	$H_2O^+ + e \rightarrow H_2O + H$	Neutralization	[103]

34	$HO_2^+ + e \rightarrow O_2 + H$	Neutralization	[103]
35	$e + O_2 \rightarrow O^- + O$	Attachment	[103]
36	$e + H_2O \rightarrow OH + H^-$	Attachment	[103]
37	$e + H_2 \rightarrow H^- + H$	Attachment	[103]
38	$e + O_2(a) \rightarrow O + O^-$	Attachment	[103]
49	$e + H_2O \rightarrow H_2 + O^-$	Attachment	[103]
40	$e + H_2O \rightarrow OH^- + H$	Attachment	[103]
41	$e + H^- \rightarrow H + 2e$	Detachment	[103]
42	$H^- + H \rightarrow H_2 + e$	Detachment	[103]
43	$H^- + O \rightarrow OH + e$	Detachment	[103]
44	$H^- + O_2 \rightarrow HO_2 + e$	Detachment	[103]
45	$OH^- + H \rightarrow H_2O + e$	Detachment	[103]
46	$OH^- + O \rightarrow HO_2 + e$	Detachment	[103]
47	$e + OH^- \rightarrow OH + 2e$	Detachment	[103]
48	$O^- + O_2(a) \rightarrow O_3 + e$	Detachment	[103]
49	$O^- + H \rightarrow OH + e$	Detachment	[103]
50	$O^- + H_2 \rightarrow H_2O + e$	Detachment	[103]
51	$O^- + O \rightarrow O_2 + e$	Detachment	[103]
52	$e + O_2 \rightarrow O_2(a) + e$	Excitation	[103]
53	$e + O \rightarrow O^1D + e$	Excitation	[103]
54	$e + O_2(a) \rightarrow O_2 + e$	Excitation	[103]

Table 9-10 Reactions between ions, metastable species and neutral molecule for SDBD plasma.

No.	Reaction	Reaction rate
1	$H + O_3 \rightarrow O + HO_2$	[103]
2	$H + HO_2 \rightarrow H_2O + O$	[103]
3	$H + HO_2 \rightarrow H_2O + O^1D$	[103]
4	$H + HO_2 \rightarrow O_2 + H_2$	[103]
5	$H + HO_2 \rightarrow 2OH$	[103]
6	$O^1D + HO_2 \rightarrow OH + O_2$	[103]
7	$O_2(a) + HO_2 \rightarrow OH + O + O_2$	[103]
8	$H + O_3 \rightarrow OH + O_2$	[103]
9	$O^1D + O_3 \rightarrow 2O_2$	[103]

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10	$O^1D + O_3 \rightarrow 2O + O_2$	[103]
11	$O^1D + H_2 \rightarrow OH + H$	[103]
12	$O^1D + O_2 \rightarrow O + O_2$	[103]
13	$O^1D + O_2 \rightarrow O + O_2(\alpha)$	[103]
14	$O^1D + OH \rightarrow H + O_2$	[103]
15	$O^1D + H_2O \rightarrow 2OH$	[103]
16	$O^1D + H_2O \rightarrow O + H_2O$	[103]
17	$H^+ + O \rightarrow O^+ + H$	[103]
18	$H^+ + H_2O \rightarrow H_2O^+ + H$	[103]
19	$H^+ + O_2 \rightarrow O_2^+ + H$	[103]
20	$H_2^+ + H \rightarrow H_2 + H^+$	[103]
21	$H_2^+ + H_2 \rightarrow H_3^+ + H$	[103]
22	$H_2^+ + H_2O \rightarrow H_2O^+ + H_2$	[103]
23	$H_2^+ + H_2O \rightarrow H_3O^+ + H$	[103]
24	$H_2^+ + O_2 \rightarrow O_2^+ + H_2$	[103]
25	$H_2^+ + O_2 \rightarrow HO_2^+ + H$	[103]
26	$H_3^+ + O \rightarrow OH^+ + H_2$	[103]
27	$H_3^+ + O \rightarrow H_2O^+ + H$	[103]
28	$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	[103]
29	$H_3^+ + O_2 \rightarrow HO_2^+ + H$	[103]
30	$O^+ + H \rightarrow H^+ + O$	[103]
31	$O^+ + H_2 \rightarrow OH^+ + H$	[103]
32	$O^+ + H_2O \rightarrow H_2O^+ + O$	[103]
33	$OH^+ + H_2 \rightarrow H_2O^+ + H$	[103]
34	$OH^+ + H_2O \rightarrow H_2O^+ + OH$	[103]
35	$OH^+ + H_2O \rightarrow H_3O^+ + O$	[103]
36	$OH^+ + O_2 \rightarrow O_2^+ + OH$	[103]
37	$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	[103]
38	$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	[103]
39	$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$	[103]
40	$O_2^+ + H_2 \rightarrow HO_2^+ + H$	[103]
41	$HO_2^+ + H_2 \rightarrow H_3^+ + O_2$	[103]
42	$O^- + H_2 \rightarrow OH^- + H$	[103]
43	$O^- + H_2O \rightarrow OH^- + OH$	[103]
44	$H^+ + H^- \rightarrow 2H$	[103]

45	$H_2^+ + H^- \rightarrow H + H_2$	[103]
46	$H_3^+ + H^- \rightarrow 2H_2$	[103]
47	$O^+ + H^- \rightarrow H + O$	[103]
48	$O_2^+ + H^- \rightarrow H + O_2$	[103]
49	$OH^+ + H^- \rightarrow H_2O$	[103]
50	$H_2O^+ + H^- \rightarrow H + H_2O$	[103]
51	$H_3O^+ + H^- \rightarrow H_2 + H_2O$	[103]
53	$H^+ + O^- \rightarrow H + O$	[103]
54	$H_2^+ + O^- \rightarrow H_2O$	[103]
55	$H_3^+ + O^- \rightarrow OH + H_2$	[103]
56	$O^+ + O^- \rightarrow 2O$	[103]
57	$O_2^+ + O^- \rightarrow O_2 + O$	[103]
58	$OH^+ + O^- \rightarrow HO_2$	[103]
59	$H_2O^+ + O^- \rightarrow O + H_2O$	[103]
60	$H_3O^+ + O^- \rightarrow H_2O + OH$	[103]
61	$H_2^+ + OH^- \rightarrow H_2O + H$	[103]
62	$H_3^+ + OH^- \rightarrow H_2 + H_2O$	[103]
63	$O^+ + OH^- \rightarrow HO_2$	[103]
64	$O_2^+ + OH^- \rightarrow OH + O_2$	[103]
65	$HO^+ + OH^- \rightarrow 2OH$	[103]
66	$H_2O^+ + OH^- \rightarrow H_2O + OH$	[103]
67	$H_3O^+ + OH^- \rightarrow 2H_2O$	[103]

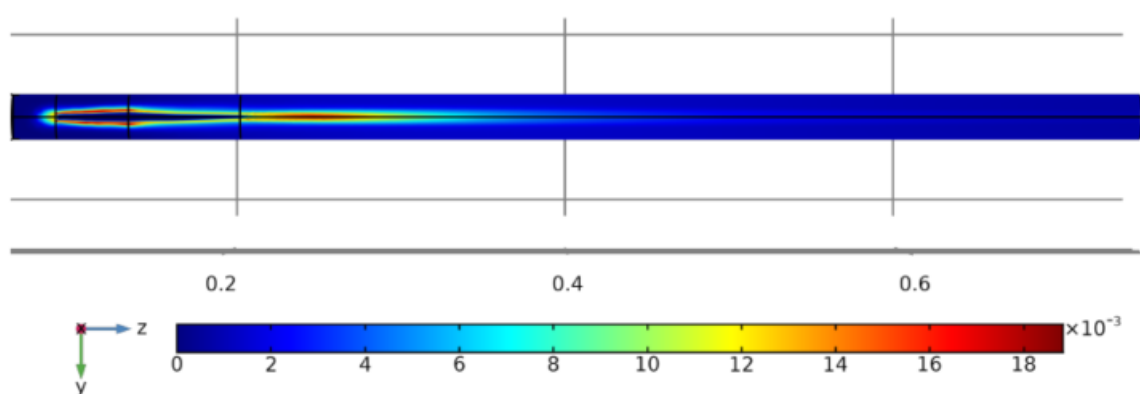


Figure 9-1 CH₃ concentration [mol/m³] for 4 vol% CH₄+Ar mix at 70 l/min in MW plasma.

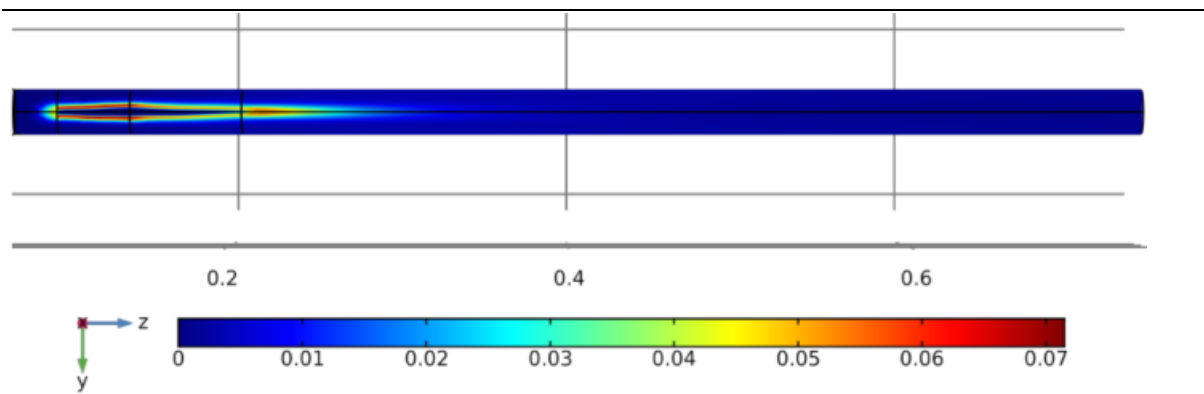


Figure 9-2 CH₂ concentration [mol/m³] for 4 vol% CH₄+Ar mix at 70 l/min in MW plasma.

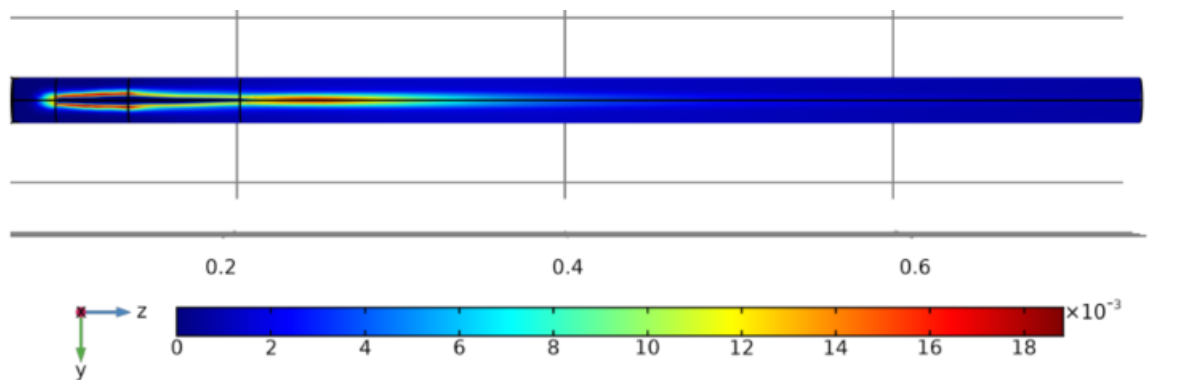


Figure 9-3 CH concentration [mol/m³] for 4 vol% CH₄+Ar mix at 70 l/min in MW plasma.

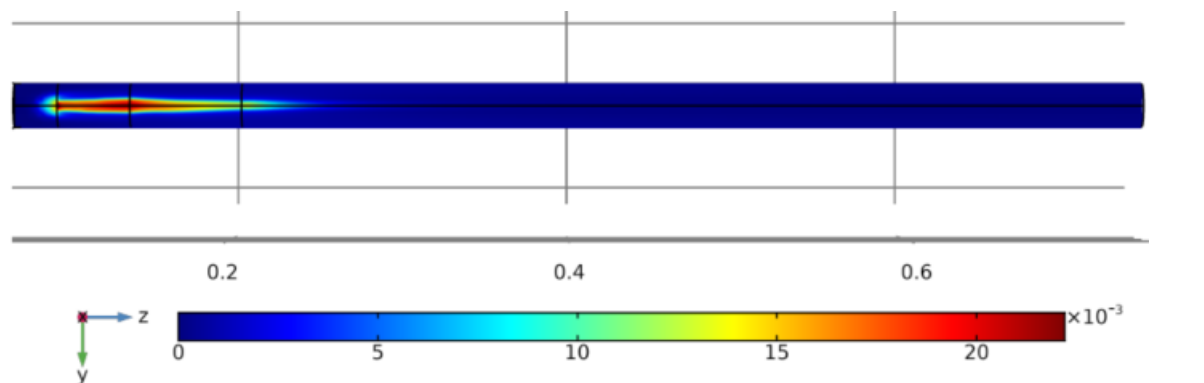


Figure 9-4 H concentration [mol/m³] for 4 vol% CH₄+Ar mix at 70 l/min in MW plasma.

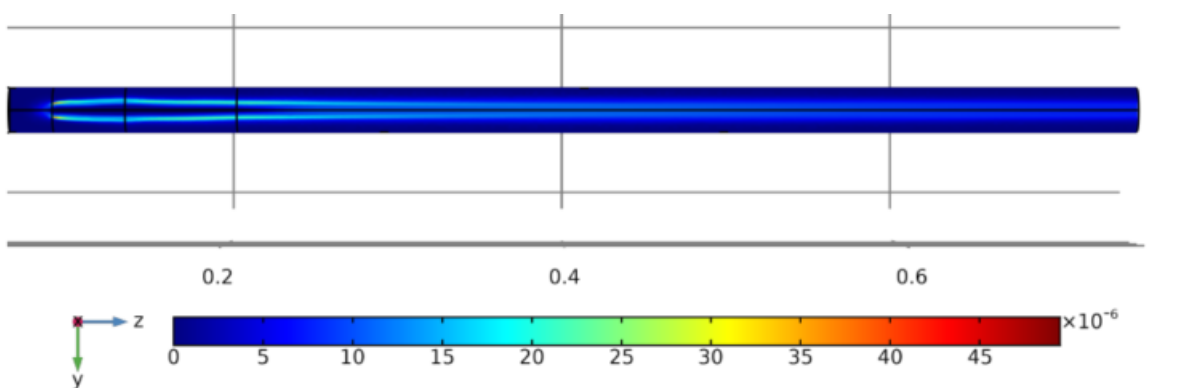


Figure 9-5 C₂H₃ concentration [mol/m³] for 4 vol% CH₄+Ar mix at 70 l/min in MW plasma.

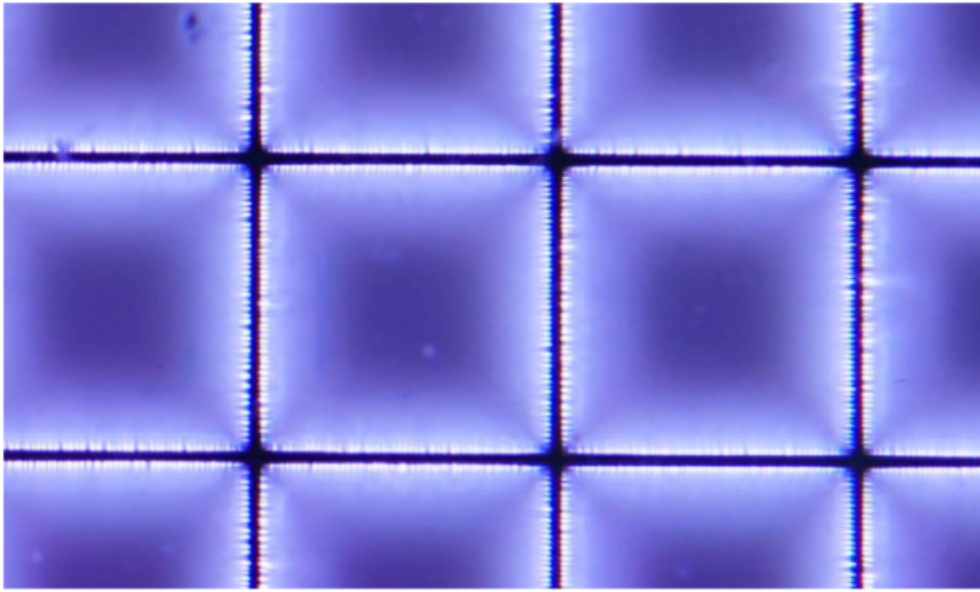


Figure 9-6 A close-up image of the SDBD plasma discharge.

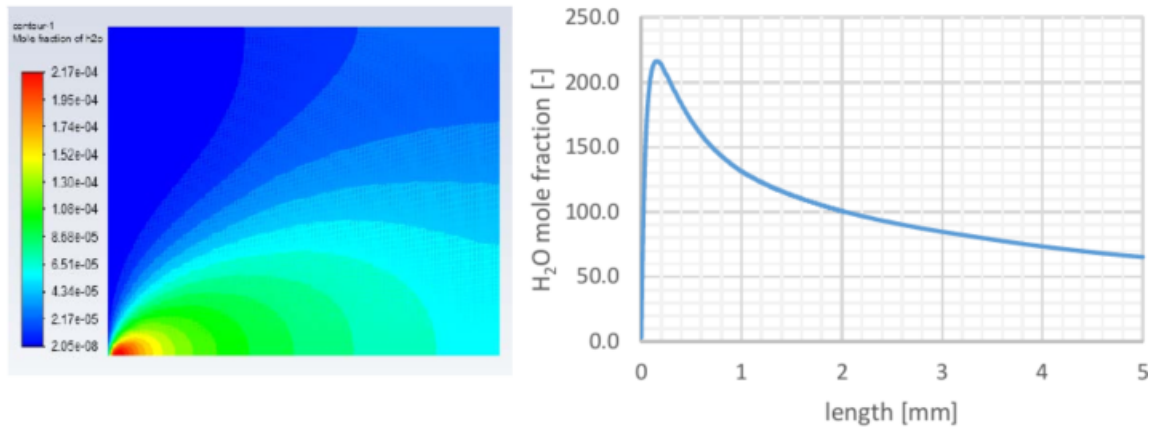


Figure 9-7 H₂O mole fraction, where $n_0(H_2O) = 0$ for SDBD plasma.

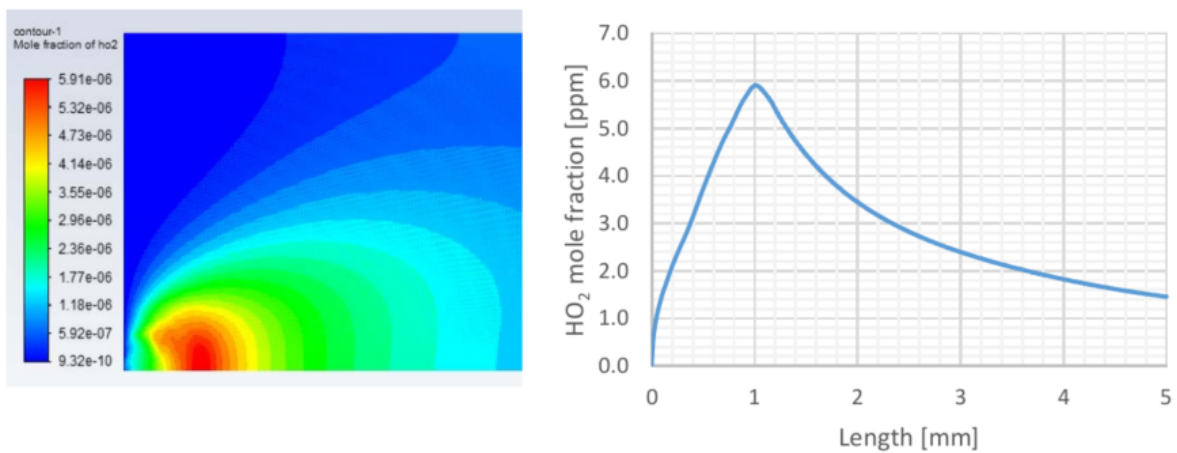


Figure 9-8 HO₂ mole fraction, where $n_0(HO_2) = 0$ for SDBD plasma.

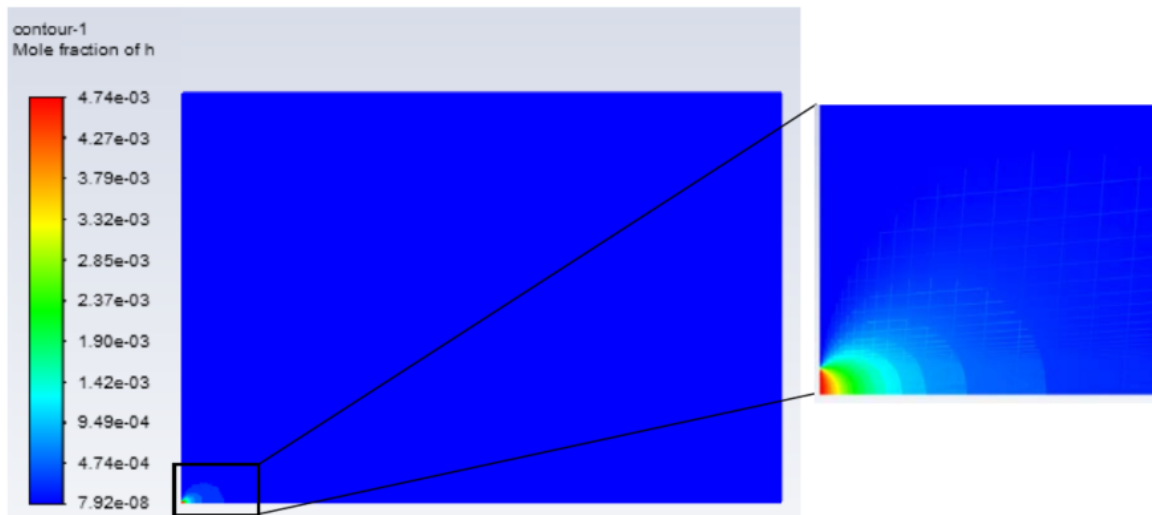


Figure 9-9 H mole fraction, where $n_0(H) = 4.8 \cdot 10^{-3} \text{ mol/mol}$ for SDBD plasma.