Non-thermal plasma discharges for methane reforming

by

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Abstract

This thesis presents the experimental study of non-thermal plasmas produced using a repetitively pulsed high voltage nanosecond discharge applied to methane partial oxidation and dry reforming at atmospheric pressure. The resulting hydrogen-containing gas is studied as a potential fuel additive to increase chemical reactivity in gas turbine engine conditions. Reactivity control is proposed as a fuel flexibility technology for low calorific fuels and as a mean to operate in low emission conditions such as lean premixed combustion. In this work, the laminar flame speed is used as an indicator of the reactivity of the fuel. Numerical simulations of 1-D laminar flames are used to calculate the laminar flame speed for different mixtures of fuel and reforming products. The results of these simulations show an increase in laminar flame speed as more reformed gas is added to the fuel. This is observed with up to 60% of inert gases in the reforming products. The composition of the reformer is calculated assuming that it reaches chemical equilibrium at high temperatures. This is similar to industrial fuel reformers, which use high temperatures and often catalysts to achieve the conversion of methane into hydrogen and carbon monoxide. The focus of this work is to explore a potentially more efficient alternative: a non-thermal plasma discharge, produced by nanosecond high voltage pulse excitation, as the driving mechanism for methane reforming, instead of the traditional high temperature process.

The experimental section of the thesis is focused on the determination of the characteristics and performance of pulsed-powered non-thermal discharge plasmas as fuel reformers. The experimental reactor consists of a pin to plane plasma chamber designed to be optically accessible and to isolate the reacting gases from the surrounding air. The designed reactor can withstand temperatures up to 1000 K. The inter-electrode distance is variable and allows control of the applied voltage of the discharge. The applied voltage pulse duration is on the order of 100 ns to prevent thermalization of the plasma channel and to decouple thermal energy

from excitation energy delivered by the discharge. When a voltage pulse is applied to the pin electrode, two stable regimes are identified: a diffuse regime with a plasma that occupies most of the inter-electrode volume, and a filamentary regime with constricted spark-like filaments. The first regime operates at a maximum energy per pulse of 1.3 mJ with negligible conversion efficiency. On the contrary, the filamentary regime reaches a maximum energy per pulse of 13.9 mJ with conversion and energy efficiencies of 26.3 % and 19.7 % respectively. Additionally, the electron number density of the filamentary regime is estimated to be 4.0×10^{17} cm⁻³ on average, while the density of the diffuse regime is more than an order of magnitude lower, at 8.9×10^{15} cm⁻³. Both regimes have gas temperatures estimated to be near 500 K, and there is no correlation with respect to the energy per pulse. These results suggest that the more energetic filamentary regime is not heating the gas, but rather delivering the energy towards better conversion efficiencies.

To study the individual contributions of reactant temperature, pulse repetition frequency, and energy per pulse on the reforming performance of the reactor, a new high voltage pulser was developed and a preheating system capable of reaching 800 K was added. The new pulser is capable of reaching 15 kV with a total pulse duration of 40 ns at a repetition rate of up to 10 kHz. With it, the energy per pulse delivered to the system is varied from 0.462 to 2.47 mJ, and the pulse repetition frequency set from 1 to 10 kHz. Similarly, with the preheating system, the inlet gas temperature is varied from 300 to 700 K. Temperature estimations show that varying the energy per pulse has a minimal effect on the temperature of the gas, while increasing the frequency heats the gas up to 777 K. In terms of reforming, increasing reactant temperature is shown to have a negligible effect, while increasing the pulse repetition frequency has the strongest effect on conversion and energy efficiency. Additionally, the best performance is observed in partial oxidation, reaching a maximum conversion efficiency of 68.2 % and an energy efficiency of 25.6 %.

The obtained results demonstrate the applicability of nanosecond repetitively-pulsed discharges as methane reformers. Capable of producing mixtures with up to 29.7 % hydrogen, these discharges can be used to increase chemical reactivity in gas turbine engine conditions as shown by the numerical simulations. This conversion is not dependent on the reactant temperature, but rather on the total amount of energy deposited by the discharge. Additionally, increasing the repetition frequency of the discharge seems to have the largest increase in efficiency, pointing towards future optimization of plasma-assisted fuel reforming technologies.

Abrégé

Cette thèse présente une étude expérimentale de plasmas non thermiques, produits par une décharge soutenue par impulsions répétées à haute tension de durée nanoseconde, appliqués à l'oxidation partielle et le reformage à sec du méthane à pression atmosphérique. Le gaz obtenu, contenant de l'hydrogène, est étudié pour son potentiel en tant qu'additif pour carburant afin d'augmenter la réactivité chimique dans les conditions propres à un moteur à turbines à gaz. L'habileté à contrôler la réactivité est proposée comme technologie permettant une plus grande flexibilité dans le choix du carburant tels que des carburants à faible pouvoir calorifique et comme moyen pour opérer dans des conditions à faible émission telles que la combustion dans des mélanges pauvres méthane-air. Dans ce travail, la vitesse de flamme laminaire est utilisée en tant qu'indicateur de la réactivité du carburant. Des simulations numériques de flammes laminaires 1-D ont été utilisées pour calculer la vitesse de flamme laminaire pour différents mélanges de carburant et produits du reformage. Les résultats des simulations montrent une augmentation de la vitesse de flamme laminaire avec une augmentation de la quantité de gaz réformé ajouté au carburant. Ceci est observé avec une proportion de gaz inertes dans les produits de reformage allant jusqu'à 60%. La composition des produits de reformage est calculée en assumant que l'équilibre chimique est atteint à haute température. La même hypothèse est utilisée pour les réacteurs industriels de reformage qui emploient des températures élevées et des catalyseurs afin de convertir le méthane en hydrogène et en monoxyde de carbone. Le travail présenté dans cette thèse se concentre sur l'exploration d'une alternative potentiellement plus efficace: une décharge plasma non thermique, produite par une impulsion à haute tension de durée nanoseconde, qui entraîne le reformage du méthane, sans avoir recours aux procédés traditionnels à haute température.

La partie expérimentale de cette thèse étudie les caractéristiques et la performance de la décharge plasma non thermique, produite par une source pulsée, utilisée pour le reformage de carburant. Le réacteur expérimental consiste en un système d'électrodes "pointe-plan", contenu dans une chambre optiquement accessible mais qui n'expose pas le système à l'air ambiant. Ce réacteur peut résister à des températures allant jusqu'à 1000 K. La distance inter-électrode est variable ce qui permet le contrôle de la tension appliquée de la décharge. La durée de l'impulsion de la tension appliquée est de l'ordre de 100 ns pour empêcher la thermalisation du conduit plasma et découpler l'énergie thermique de l'énergie d'excitation délivrée par la décharge. Lorsqu'une impulsion de tension est appliquée à l'électrode en pointe, deux régimes stables sont identifiés: un régime diffus avec un plasma qui occupe la majorité du volume entre les électrodes et un régime filamentaire présentant des filaments serrés ressemblant à des étincelles. Le premier régime opère à une énergie maximale par impulsion de 1.3 mJ et a un rendement négligeable. Par contre, le régime filamentaire atteint une énergie maximale par impulsion de 13.9 mJ et présente un rendement de 26.3 % et une efficacité énergétique de 19.7 %. De plus, la densité électronique du régime filamentaire est estimée à 4.0×10^{17} cm⁻³ en moyenne, alors que la densité dans le régime diffus est à plus d'un ordre de grandeur au-dessous à 8.9×10^{15} cm⁻³. La température du gaz des deux régimes se situe autour de 500 K et il n'y a pas de corrélation avec l'énergie par impulsion. Ces résultats suggèrent que le régime filamentaire qui est plus énergétique ne réchauffe pas le gaz, mais que l'énergie délivrée est plutôt utilisée pour augmenter le rendement.

Afin d'étudier les contributions individuelles de variables telles que la température des réactifs, la fréquence de répétition de l'impulsion et l'énergie par impulsion sur le procédé de reformage dans ce réacteur, un nouveau générateur d'impulsions à haute tension a été développé et un système de préchauffage capable d'atteindre 800 K a été ajouté. Ce nouveau générateur peut atteindre 15 kV pour une durée totale d'impulsion de 40 ns à une fréquence de répétition allant jusqu'à 10 kHz. L'énergie par impulsion livrée au système varie entre 0.462 et 2.47 mJ. La fréquence de répétition de l'impulsion est réglée entre 1 et 10 kHz. Avec le système de préchauffage, la température du gaz entrant peut être choisie entre 300 et 700 K. Les températures estimées indiquent que l'énergie par impulsion a peu d'effet sur la température du gaz, tandis qu'augmenter la fréquence augmente la température du gaz jusqu'à 777 K. Il a été démontré que l'augmentation de la fréquence de répétition de l'impulsion avait le plus fort effet sur la conversion et l'efficacité énergétique. De plus, la meilleure performance a été observée dans des conditions d'oxidation partielle, atteignant un rendement maximal de 68.2 %

et une efficacité énergétique de 25.6 %.

Les résultats obtenus démontrent qu'il est possible d'utiliser des décharges soutenues par impulsions répétées de durée nanoseconde pour le reformage du méthane. Capables de produire des mélanges contenant jusqu'à 29.7 % d'hydrogène, ces décharges peuvent être utilisées pour augmenter la réactivité chimique dans les conditions propres à un moteur à turbines à gaz tel que démontré dans les simulations numériques. Cette conversion ne dépend pas de la température des réactifs, mais plutôt de la quantité totale d'énergie délivrée par la décharge. De plus, l'augmentation de la fréquence de répétition de l'impulsion de la décharge semble causer la plus grande augmentation en efficacité, guidant ainsi des travaux futurs d'optimisation des technologies de reformage de carburant assistées par plasma.

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Introduction

1.1 Problem Statement

Since the beginning of the industrial age, our society has become progressively more dependent on the combustion of hydrocarbons to supply its energy demands. Technology has advanced in parallel, always in the direction of increasing process efficiency, driven mainly by economic or ecological incentives. However, the combustion of hydrocarbons comes with the well-known drawback of pollutant emissions, which has driven the environment to its current critical state. Nowadays, it is a global priority to find solutions to reduce pollutant and greenhouse gas effect emissions like carbon dioxide. This has prompted an increase in emission regulations for combustion processes, directly affecting power generation. Moreover, with rising energy demands, there has been an increased interest in alternative, renewable and clean energy sources.

Burning hydrocarbons in gas turbine engines is a common process for power generation. Typical pollutants emitted are nitric oxides (NO_x) , carbon dioxide (CO_2) , carbon monoxide (CO), unburnt hydrocarbons, particulate matter and volatile organic compounds (VOCs). Several technologies have been developed to reduce pollutant emission, one of which is

1.1 Problem Statement

lean-premixed combustion. It consists of burning fuel with an excess of air, ensuring all fuel is burnt, preventing the emission of unburnt hydrocarbons or particulate matter, and lowering the flame temperature, which reduces pollutant emissions like NO_x . However, as the fuel-air mixture is made leaner, the reactivity and consequently the speed of the flame are reduced. When the flame speed is reduced enough to produce combustion instabilities, blow-out may occur. This is especially important in transient operation regimes, where the power output is varied, potentially leading to low reactivity conditions and flame extinction. Additionally, some renewable fuels might be unsuitable to operate at these low-emission conditions. For instance, biogas, which is a product of organic decomposition, is a diluted fuel with lower energy content and reactivity. A solution to increase the flame speed, and consequently enhance the reactivity of the fuel-air mixture, is the addition of hydrogen to the fuel stream [1, 2, 3].

Nowadays, hydrogen is mainly produced as one of the main constituents of synthesis gas (syngas) through methane reforming [4, 5]. Syngas also finds a variety of uses in industry, from the synthesis of higher order hydrocarbons [6, 7] to power generation in solid-oxide fuel cells [8, 9, 10]. There are three main methane reforming processes that differ on the coreactant used: steam reforming (CH_4-H_2O), partial oxidation ($2CH_4-O_2$) and dry reforming (CH_4-CO_2). These techniques typically require external heaters to achieve temperatures in excess of 1000 K, which make assemblies bulky, require specialized and expensive materials, are slow to start-up, and do not handle load changes efficiently [5]. They are often used in conjunction with transition metal catalyst to increase the thermal efficiency [4, 11, 12, 13]. However, catalytic processes are still bound to high temperatures, and catalyst deactivation by coke deposition is a challenge for this technology [14, 4]. In this work, we explore the applicability and reforming performance of non-thermal plasmas as an alternative to catalytic processes.

Plasmas are quasineutral ionized gases composed of a mixture of ions, electrons and neutrals. There are many plasmas sources, but for chemical processing applications they are

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typically produced by applying an electric field into a neutral gas. The potential gradient accelerates electrons and ions, which collide with other particles present in the gas. In fact, plasma technologies are attractive for fuel reforming due to their ability to dissociate molecules and produce highly reactive species through electron impact [15, 16, 17, 18]. While charged particles gain a high kinetic energy in a relatively short time due to the presence of an electric field, the neutral particles that compose the majority of the gas remain close to their initial temperature. These are known as non-thermal or non-equilibrium plasmas. If the charged particles have enough time to transfer their energy to the neutrals, equilibrating the temperature of the plasma, it becomes a thermal or equilibrium plasma.

Thermal plasmas have been studied as fuel reformers, obtaining high methane conversion efficiencies [19, 20]. Their high energy density allows this technology to be compact and to respond fast to changes. However, thermal plasmas also require very high energy inputs, most of which is wasted in gas and electrode heating, making some of these inefficient when compared to traditional thermochemical reactors [21]. Conversely, non-thermal plasmas are more efficient for fuel reforming [22]. Since the gas remains at low temperature, the energy is spent mostly on species excitation. Nowadays there are many different electrical discharges that can sustain a non-thermal plasma at atmospheric pressure. Three that are widely used in the field are: dielectric barrier discharges (DBDs) [23, 24, 25], gliding arcs [26, 27, 28], and nanosecond repetitively pulsed (NRP) discharges [29, 30, 31, 32, 33].

Nanosecond repetitively pulsed discharges have recently shown promising results for fuel reforming and CO₂ splitting [29, 30, 31, 32, 33, 34, 35]. These discharges are produced by voltage pulses ranging from tens of thousands [36] to hundreds of thousands of volts [37], delivering instantaneous power levels on the order of tens of kilowatts in a few nanoseconds. The discharge produces a pool of highly reactive species in a plasma with a high degree of disequilibrium. These conditions produce a highly reactive plasma, which can be used to drive

reforming reactions. The experimental work presented in this dissertation provides the design, validation, and characterization of nanosecond repetitively pulsed discharges used for methane reforming.

1.2 Objectives

Hydrogen is known to produce an increase in the speed at which a flame propagates into unburned reactants when used as an additive for combustible mixtures [1, 2, 3]. However, when produced through reforming processes, hydrogen is obtained from syngas, which has many other components depending on the process use, some of which are diluents. The first objectives provide an answer to the question if hydrogen diluted with other gases in syngas is still capable of producing the desired reactivity enhancement. The next objectives address the characteristics of high-voltage pulsed discharges as means to produce a reforming plasma and their capabilities to produce hydrogen containing gases. The last objective determines which parameter should be varied to obtain the highest increase in reforming efficiency. The specific objectives that were completed in this thesis are the following:

- 1. To determine if the composition of gas turbine engine exhaust gases is applicable as a coreactant for partial oxidation of methane;
- 2. To study the effect of syngas addition to methane and biogas for reactivity enhancement of fuel-air mixtures at gas-turbine-engine-relevant conditions;
- To study the characteristics and the different regimes observed in a non-thermal plasma produced by an atmospheric pressure high-voltage nanosecond repetitively pulsed discharge for methane reforming;
- 4. To quantify the reforming efficiency of the discharge;
- 5. To determine which parameter has the greatest influence in the reforming efficiency.

1.3 Thesis Structure

This is a manuscript-based thesis with introductory chapters covering background theory and methodology. Chapter 2 consists of a comprehensive summary of the background and theory required to execute the work presented in this dissertation. It covers topics on combustion fundamentals, plasma engineering, fuel reforming, optical emission spectroscopy, and a literature review on plasma-assisted fuel reforming. Chapter 3 is a thorough description of the methodology and procedures followed to carry out the numerical simulations and experiments presented in each manuscripts. The bulk of the thesis consists of two published manuscripts and one in preparation for submission, which follow the objectives previously stated. Each chapter includes a preface with a brief summary outlining the connection with previous and subsequent chapters. Chapter 4 is titled A Numerical Study on the Reactivity of Biogas/Reformed-Gas/Air and Methane/Reformed-Gas/Air Mixtures at Gas Turbine Relevant Conditions, which was published in ASME Turbo Expo 2016: Turbomachinery Technical Conference and Exposition, and addresses objectives (1) and (2). Chapter 5 addresses objectives (3) and part of (4), and was published under the title Regimes of an atmospheric pressure nanosecond repetitively pulsed discharge for methane partial oxidation, in the Journal of Physics D: Applied Physics. Chapter 6 is in preparation for submission to a special issue of the Journal of Physics D: Applied Physics, under the title of Energy Efficiency of a Nanosecond Repetitively Pulsed Discharge for Methane *Reforming*, and addresses objective (4) in part and objective (5).

2

Background and Theory

This chapter presents the concepts and theory used throughout this thesis. It is a summary of fundamental knowledge from several fields that go from combustion science to plasma physics. It includes basic and well-established science, as well as cutting-edge knowledge from up-to-date literature review. However, concepts covered in manuscripts presented in later chapters are not repeated.

2.1 Reaction Thermodynamics

The numerical study presented in this thesis uses basic concepts of reaction thermodynamics to model a theoretical gas turbine engine and fuel reformer. The following subsections present chemical reaction fundamentals, such as chemical equilibrium, reaction kinetics, ignition delay time and laminar flame speed. It is based on the work of Law [38], who is cited only here to avoid the repeated use throughout this section.

2.1.1 Chemical Equilibrium

A reactive multi-component system reaches chemical equilibrium when the concentration of both its reactants and products have no further tendency to change. The description of this state is given by chemical thermodynamics, which is the foundation of the science behind combustion and fuel reforming technologies. The state of chemical equilibrium is an important concept as it predicts the composition and temperature of the final state that a system can reach. The tendency of reactants and products to remain constant when chemical equilibrium is reached can be described with the following expression:

$$\sum_{i=1}^{m} \mu_i \mathrm{d}N_i = 0, \tag{2.1}$$

where μ_i is the chemical potential per molecule, and N_i is the number of molecules of species *i*. The chemical potential μ_i is defined as the change in the Gibbs energy of the system *G*, as the moles of species *i* are changed while the rest of the species, temperature, and pressure are kept constant. Mathematically μ_i and *G* are expressed as:

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right) \quad \text{where} \quad G = H - TS,$$
(2.2)

where T is the temperature, and H and S are the total enthalpy and entropy of the system respectively. From Equation 2.2, it is clear that the minimization of the Gibbs energy satisfies the condition in Equation 2.1. The definition of the Gibbs in energy Equation 2.2 shows that its minimization results from the minimization of the total enthalpy and maximization of the total entropy. These two are opposing tendencies in terms of the composition of the final products. A minimum H results in more stable products like H₂O and CO₂. On the contrary, S increases with increasing number of products, even though it means the production of energetically unfavorable

2.1 Reaction Thermodynamics

species, like 2H instead of H_2 . At equilibrium, there is a trade-off between these two processes leading to a finite number of dissociated species among other stable molecules. Figure 2.1 shows the schematic of this behavior and how the Gibbs energy reaches a minimum at equilibrium.



Figure 2.1: The total enthalpy H, entropy S, and the Gibbs energy G as a function of the product composition.

Minimizing the Gibbs energy for a multicomponent system becomes a complicated task as more species are involved, and is often done by a computer. For instance, Cantera is a free and open-source software capable of calculating the minimum Gibbs energy and determining the equilibrium state of many reactive mixtures, including multiphase systems. This is the main procedure used in this thesis when estimating final compositions and temperatures, in reactors and flames. In fact, Chapter 4, uses this methodology extensively to determine the composition and temperature of a mixture after a theoretical fuel reformer. Figure 2.2 shows an example of this technique and the estimated compositions at different gas temperatures for methane pyrolysis and the two reforming reactions used in this thesis.



Figure 2.2: Equilibrium compositions as a function of the reactant temperature T_{gas} at atmospheric pressure.

Figure 2.2 demonstrates the usefulness of this technique in estimating the product composition of different reactions. For instance, it shows the nonintuitive result of mixing methane with carbon dioxide. Water and solid carbon are not the expected products from the mixture of these two at room temperature. It also shows that it requires up to 3000 K to have hydrogen and carbon monoxide only as products. However, this technique disregards the time needed to reach the equilibrium state. It may take many years to reach equilibrium and have water and solid carbon present in the products for methane and carbon dioxide mixtures. This is studied by looking at the conversion rates of the reacting mixtures, which is discussed in the next subsection.

2.1.2 Chemical Kinetics

Chemical equilibrium is an adequate assumption to estimate the composition and temperature of systems where enough time has passed. However, many real systems cannot reach chemical equilibrium because the conversion from reactants to products are dependent on finite rates. For instance, if methane and oxygen were put together in a reactor at room temperature no reaction

2.1 Reaction Thermodynamics

would be observed, even if chemical equilibrium predicts a mixture of water and carbon dioxide. This is true as long as there is no ignition source, in which case the now faster reaction rates would push the conversion into perceivable time scales.

The rate of a reaction depends on the number of collisions between particles that have enough energy to break existing bonds and form new ones. This can be mathematically described by the collision frequency and the concentration of the reactants or products. The expression is known as the law of mass action and it is:

$$\omega_{\rm f} = k_{\rm f} \prod_{i=1}^m c_i^{v_i'},\tag{2.3}$$

where ω is the reaction rate, c_i and v_i are the concentration and the reaction coefficients of species *i*, *m* is the number of reactants or products, and k_f forward reaction rate constants. Products can also be converted back into reactants; the process is described by the law of mass action but with a backward reaction rate constant k_b . The net reaction rate ω is then simply the difference between ω_f and ω_b . Both forward and backward reaction rate constants *k* are dependent on the number of collisions between species with enough energy to make the reaction happen, known as the activation energy E_a . This is represented by the Arrhenius equation:

$$k = A \cdot e^{\left(\frac{-E_a}{RT}\right)},\tag{2.4}$$

where A is the pre-exponential factor, and R is the universal gas constant. Equation 2.4 can be derived analytically from collision or transition-state theory. The main difference between each derivation is the definition of the activation energy E_a and the pre-exponential factor A. However, for complex systems such as plasma driven reactions, the pre-exponential factor, the reaction rate constants and the reactivity are mainly obtained empirically.

2.1.3 Ignition Delay Time

Although eventually the reaction takes place, mixtures of methane and air at room temperature and atmospheric pressure remain unreacted for considerably large timescales. However, if the temperature is increased, the mixture reaches a point where the reaction rate increases enough to see the ignition of the mixture in a few seconds. The time it takes for a combustible mixture to ignite is called the ignition delay time τ_{ign} . For an adiabatic system, it can be shown that:

$$\tau_{\rm ign} = \frac{C_v(RT^2/E_a)}{q_c\omega_{\rm u}},\tag{2.5}$$

where C_v is the gas heat capacity at a constant volume, q_c is the heat of reaction per mole of fuel, and ω_u is the reaction rate of the unburnt mixture. Equation 2.5 shows that τ_{ign} is inversely proportional to ω_u . This means that τ_{ign} can be used to characterize the reactivity of the fuel-air mixture at conditions before entering the reaction zone of a flame. This is also a useful parameter to determine if a reactive mixture auto-ignites before reaching the combustor of a gas turbine engine. A detailed analysis of this technique is available in Chapter 4.

2.1.4 Laminar Flame Speed

A laminar flame is a self-propagating localized combustion zone. Within a stationary premixed flammable mixture, a flame freely propagates with a certain burning velocity from one point to another. However, if the mixture is flowing with the same speed as the flame propagation speed, the flame can be stabilized so that it is stationary in the laboratory reference frame. The propagation of the flame is caused by the preheating of the incoming reactants by the exothermic reaction of the flame itself. Figure 2.3 shows the schematic of a laminar flame propagating into an unburned methane-air mixture at 1 atm and 300 K.



Figure 2.3: Schematic of a stoichiometric methane-air laminar flame at 1 atm and 300 K, showing species concentration, temperature and heat release. Obtained from a 1-D laminar flame simulation using Cantera.

Three zones are identifiable in the previous figure, a preheat zone where the adjacent flame increases the temperature of the incoming reactants, the reaction zone where the flame is located, and the downstream region which contains the products at the post-flame temperature. Preheated reactants eventually reach an ignition temperature T_{ign} , which marks the end of the preheat zone. The reaction zone is characterized by a rapid heat release, an increase in the forward global reaction rate and the conversion of the incoming reactants. After it, in the downstream direction, the products are at the post flame temperature T_b , and the product composition is near that of equilibrium due to the high reaction rates at the flame. The reaction rate at the flame location $\dot{\omega}_b$ is greater than the reactivity of the unburned mixture $\dot{\omega}_u$, which is inversely correlated to the ignition delay time. The reactivity evaluated at flame temperature, and the rate of thermal diffusion α_t , are controlling factors of the flame propagation speed or laminar flame

2.1 Reaction Thermodynamics

speed $S_{\rm L}$. This proportionality can be expressed mathematically as:

$$S_{\rm L} \propto \sqrt{\alpha_{\rm t} \dot{\omega}_{\rm b}}$$
 (2.6)

Although $S_{\rm L}$ depends on $\dot{\omega}_{\rm b}$, the reactant initial temperature $T_{\rm u}$ does have an influence on this parameter. This is because the flame reaches higher $T_{\rm b}$ for higher $T_{\rm u}$. The laminar flame speed, $S_{\rm L}$, also depends on the chemistry of the mixture, which can be observed if evaluated at different equivalence ratios ϕ . Figure 2.4 shows the influence of chemistry and temperature on the laminar flame speed of a methane-air mixture at 1 atm. It shows that mixtures near stoichiometry result in the higher $S_{\rm L}$. Similarly, increasing $T_{\rm u}$ produces an increase in $S_{\rm L}$. A detailed analysis of the effects of chemistry and temperature on $S_{\rm L}$ is explored in Chapter 4



Figure 2.4: Laminar flame speed of methane-air with respect to the equivalence ratio at 1 atm and various mixture temperatures. Obtained from a 1-D laminar flame simulation using Cantera.

2.2 Fuel Reforming

2.2.1 **Reforming reactions**

Methane is a stable molecule that needs high energy inputs to dissociate and reform into new products. In fuel reforming, a high temperature is the traditional mean to deliver enough energy [5] to drive endothermic reactions such as steam reforming, dry reforming and methane thermal decomposition, and exothermic reactions like partial oxidation. The relative content of hydrogen to carbon monoxide in the reforming products depends on the method used, and it is chosen depending on the application.

Methane thermal decomposition involves the complete dehydrogenation of methane, producing only solid carbon and hydrogen. The process is described by:

$$CH_4 \to C(s) + 2H_2 \qquad \Delta H^0_{298 \,\mathrm{K}} = 75 \,\mathrm{kJ/mol.}$$
 (2.7)

Thermal decomposition of methane requires 75 kJ/mol to take place, as seen in Equation 2.7. Typically, in the absence of a catalyst, this is carried out at temperatures in excess of 1500 K. Catalysts are used to lower this temperature, and current efforts are aimed at increasing its efficiency. The reaction produces only hydrogen as a gaseous product, making it ideal for low carbon dioxide storage of renewable energy such as solar. However, this also means that the leftover carbon progressively deactivates the catalyst [39, 40]. Besides being applicable for a reforming process by itself, this reaction is also observed in other reforming processes, especially dry reforming [41]. In some, the dehydrogenation of methane is actually the rate determining step [24], so the study of this reaction is of interest for all reforming technologies.

Steam reforming is industrially used on a large scale for hydrogen production [4, 5]. It

involves the reaction of methane and water as:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0_{298 \,\text{K}} = 206 \,\text{kJ/mol.}$$
 (2.8)

Reaction 2.8 produces three times more hydrogen than carbon monoxide, which makes it ideal for applications where a high hydrogen concentration is needed, such as ammonia synthesis. It typically happens over a transition metal catalyst at temperatures exceeding 1000 K [5]. An intermediate reaction in steam reforming is water-gas shift, where carbon monoxide and water react to produce carbon dioxide and hydrogen. For temperatures at which steam reforming takes place, water-gas shift reaction rates are fast and are typically at chemical equilibrium. Although the stoichiometric reaction of steam reforming is 1:1 methane to steam, it usually happens in excess of water to promote water-gas shift reaction, boosting the production of hydrogen over carbon monoxide [42].

Partial oxidation produces a less hydrogen-concentrated syngas by reacting methane with oxygen:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0_{298\,\text{K}} = -36\,\text{kJ/mol.}$$
 (2.9)

Although reaction 2.9 is exothermic, it needs to have its reactants heated to overcome the activation energy. Partial oxidation occurs at high temperatures, which also exceed 1000 K [43, 44]. The process involves the production of low amounts of water and carbon dioxide. However, most of these occur during intermediate steps, and end up reacting with any methane present in the mixture. A transition metal catalyst enhances the overall process, allowing the reforming to occur with less preheating of reactants and at lower overall temperatures [43]. Partial oxidation has lower hydrogen output per mole of methane compared to steam reforming, thus having lower efficiency for hydrogen generation applications [44]. However, the technology allows for rapid start-up, responds well to load change, and works at high pressures [42]. It is possible to

use air instead of pure oxygen, foregoing the separation process, but having the effect of nitrogen dilution. Nevertheless, results with rare earth oxide catalysts show conversion efficiencies in excess of 90 % at 1000 K [45] and up to 94 % hydrogen yield using nickel-based catalysts at 1050 K [46].

Similarly to steam reforming, dry reforming is an endothermic reaction, but instead of water, methane reacts with carbon dioxide:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298\,\text{K}} = 247\,\text{kJ/mol.}$$
 (2.10)

Equation 2.10 is an interesting reaction from an environmental point of view as it consumes two greenhouse gases in the production of valuable energy carriers. Similarly to previous endothermic reactions, dry reforming requires very high temperatures to drive the reaction [47, 41]. In fact, autothermal reformers are recommended for this process, partially or completely oxidizing methane to produce the required heat [48]. Catalysts are often used for dry reforming as well, to lower this temperature requirement. However, this process is inevitably accompanied by carbon deposition, even at high temperature [49, 50].

Reforming processes are often carried out using a very diverse selection of catalysts, which currently are an area of interest in the scientific community. The main purpose is to lower the required temperature to drive the reactions forward and thus to increase the overall efficiency of the process [4, 11, 12, 13, 43, 44]. However, the challenge of catalytic processes for fuel reforming is carbon deposition, and part of the research is dedicated at mitigating this drawback [4, 49, 51, 52]. In this work, we explore non-thermal plasmas as an alternative to catalytic processes to achieve conversion at relatively low reactant temperature. The framework and current understanding of plasma processes are explained in the subsections that follow.

A plasma is an ionized gas in which the bulk net charge is zero, a condition also known as quasineutrality. It is a mixture of neutral and charged species, namely electrons and ions, which confer the gas high conductivity. Depending on their particles temperature, a plasma can be classified as thermal or non-thermal plasma. Electrons have a small mass compared to other particles, such as ions and neutrals. During a discharge, electrons start moving through the imposed electric field, having a mean velocity different from the heavier ions and neutrals. Pressure, overall temperature, and electrical characteristics of the plasma dictate if this condition can be maintained in steady state. This is known as a non-equilibrium plasma. If there are enough collisions that allow electrons to thermalize ions and neutrals, equilibrating the temperature between particles, the plasma becomes thermal or at equilibrium [15, 53].

Transient non-equilibrium plasma is the driving mechanism through which methane reforming is carried out for the experiments described in this thesis. The following subsections present the fundamentals of non-equilibrium plasma and the different breakdown mechanisms of a discharge. It is based on the works of Fridman [15] and Raizer [53], and similarly to the previous section, the citations remain only here. The high-voltage nanosecond pulsed discharges used for methane reforming are produced through avalanche-to-streamer transition for the volumetric diffuse regime, and streamer-to-spark transition for the filamentary regime.

2.3.1 Electron Avalanche

When an electric field E_0 is applied into a gas, any free charged particle starts moving towards the electrode with the opposite charge. Electrons, which are lighter than neutrals or ions, move faster and start to collide with other species. A fraction of these collisions has enough energy to ionize the colliding partner. The ionization process means that a new electron has been

produced that can be accelerated as well. The newly created electron continues the process and collides with other particles, creating more electrons as more particles are ionized. This electron multiplication process is known as the electron avalanche, and precedes any breakdown mechanism. However, not only ionization collisions can occur, some collisions result in the recombination of the ion and the electron. The electron multiplication and recombination rates per unit length can be described by the Townsend coefficients in the following expressions:

$$\alpha = \frac{k_{\rm i}(E/N)}{\mu_{\rm e}(E/N)}, \quad \beta = \frac{k_{\rm r}(E/N)}{\mu_{\rm e}(E/N)}, \tag{2.11}$$

where k_i and k_r are the ionization and recombination rate constants, and μ_e is the electron mobility. All parameters are dependent on the reduced electric field E/N, which is the electric field E divided by the gas number density N, and has units of Townsends (Td).

Figure 2.5 shows the schematic of an electron avalanche and the electric fields that act on it. Electrons in the avalanche move with a drift velocity in the direction of E and a magnitude equal to $\mu_e E$. Additionally, there is radial diffusion of electrons which makes the avalanche grow radially. Electrons are located at the avalanche head, leaving a tail of ions as the avalanche moves to the anode. Ions are concentrated near the avalanche head, next to the electrons, decreasing in the axial direction towards the cathode exponentially, and in the radial direction with the same Gaussian profile as the electrons.

Due to the space charge in the avalanche, a dipole forms with a characteristic length of $1/\alpha$, and produces an electric field E' as depicted in Figure 2.5. The dipole electric field E' added to the imposed field E_0 results in a total field E acting over the avalanche. The resultant electric field is amplified in both the head and behind the avalanche before the avalanche reaches the anode, accelerating the ionization rate. Once the avalanche reaches the anode as seen in Figure 2.5 (right), the electrons are consumed by it, leaving only the ions in the avalanche tail

behind. The accumulation of positive charges produces a field much higher than the original imposed field E_0 , having a maximum E at a characteristic distance $1/\alpha$.



Figure 2.5: Schematic of the electron avalanche prior to (left) and once it reaches the anode (right), adapted from [53].

2.3.2 Streamer Discharge

The resultant electric field E acting on an electron avalanche is higher than the original imposed field E_0 . If E is at least ~ $2E_0$, or if E' is approximately equal to E_0 then the avalanche transits to the streamer phase. This is the generalized criterion for streamer formation. This can be evaluated using the Meek breakdown criteria, which involves using the avalanche amplification parameter αd , where d is the inter-electrode distance, as:

$$\alpha d \ge 20, \quad \text{or} \quad N_e = e^{\alpha d} = 3 \times 10^8.$$
 (2.12)

To reach the required electron number density N_{e} , the applied voltage has to be sufficiently high to induce an intense electric field that is capable of producing enough electron

multiplication near the anode surface. Once the streamer forms, it propagates according to the reduced electric field in its head. A streamer can propagate from cathode to anode or vice versa. Figure 2.6 (left) shows a schematic of a cathode-directed streamer which is produced when the transition happens after the avalanche reaches the anode. Conversely, Figure 2.6 (right) shows an anode-directed streamer, produced before the avalanche reaches the anode by means of very high and fast applied voltages. Streamers emit high-energy photons which produce secondary electron avalanches near the streamer head through photoionization. The electrons in the secondary avalanche are pulled into the primary avalanche, creating a quasineutral channel. The electron feed from the secondary avalanches is the propagation mechanism of the streamer discharge.

The propagation of the streamer is mainly limited by recombination collisions. At pressures lower than atmospheric, streamers can reach propagation speeds well above 10^8 cm/s. As pressure and gas density are increased, the number of recombining collisions increases while the electric field at the streamer head stays relatively constant, effectively decreasing the streamer propagation speed. Also, it has been observed that when atmospheric pressure is reached, primary and secondary streamers exist in transient high voltage discharges [54]. The primary streamer propagates fast with a high E/N characteristic of the streamer head. Collisions with the primary streamer produces highly energetic particles and ions. On the other hand, the secondary streamer is slower as it propagates with lower values of E/N, and only occurs if a voltage persists at the anode. The slower streamer produces less energetic species, but in greater numbers as it lasts longer.

The inelastic collisions of heavy species with electrons results in a high degree of thermal disequilibrium, where vibrational and electronic temperatures exceed the translational temperature of the gas. The highly energetic species produced from this collisions in the streamer create a highly reactive environment that is of interest for gas processing applications,


Figure 2.6: Schematic of a cathode-directed (left) and an anode-directed streamer (right), adapted from [53].

such as fuel reforming [16, 17, 18, 55]. This transient behavior allows chemical processing without spending energy in bulk gas heating, which could increase the efficiency of chemical processing. Moreover, for processes where temperature is critical, such as gas turbine engine combustion where NO_x emissions depend on the flame temperature, this type of discharges could be applied [56]. However, since the density of reactive species produced in the streamer is low, to produce a usable pool of particles, the repetition frequency of the discharge needs to be high. For this thesis, streamer discharges produce the diffuse regime in methane and methane-oxidizer mixtures, and are thoroughly described in Chapter 5.

2.3.3 Spark Discharge

Figure 2.7 is a schematic of the evolution of different parameters and properties of a streamer discharge as it transits into a spark. The process starts with a positive glow corona, as shown in Figure 2.7 (a). From Figure 2.7 (b) to (f), the schematic shows the evolution of the streamer as described in the previous subsection, including the formation and propagation of the secondary

2.3 Plasma Fundamentals

streamer. In Figure 2.7 (f), the secondary streamer is propagating from anode to cathode accompanied by an increase in E/N and gas expansion at the streamer tail. If the applied field E_0 persists above a certain critical value of E/N after the secondary streamer has reached the cathode, there is a streamer-to-spark transition, as shown in Figure 2.7 (h). Once the plasma channel is formed, a high degree of ionization and gas expansion accompanies the spark formation.



Figure 2.7: Schematic of the streamer-to-spark transition (top), and the conduction current of the discharge (bottom), adapted from [57].

The streamer-to-spark transition involves an ionization back-wave that is responsible for the high degree of ionization in the plasma channel. This process starts as the primary streamer approaches the cathode. The intense electric field at the head of the primary streamer leads to electron emission from the cathode, leading to rapid electron multiplication and an ionization front propagating along the residual streamer channel towards the anode. As this wave passes through the channel, the degree of ionization is greatly increased until it reaches the electrode. Once the anode is reached, the spark transition is complete. The high degree of ionization

2.3 Plasma Fundamentals

increases the electrical conductivity of the plasma channel, resulting in a rapid current increase, which is characteristic of the spark regime.

The higher conductivity of the plasma channel produces a collapse in the applied voltage and an increase in the current. This process is accompanied by heating of the plasma channel and expansion of the gas. Heating is produced as the energy delivered by the discharge cannot be removed as fast as it is added, increasing the temperature of the filament very rapidly, at about $\sim 50 \text{ K/ns}$ [58]. The expansion of the gas in the filament produces a drastic change in pressure with an associated hydrodynamic shockwave, which expands outward radially [59, 60]. Characterization of this regime is described in Chapter 5, and a thorough analysis of the influence of the energy delivered per pulse, repetition frequency, and reactant temperature on the spark characteristics is given in Chapter 6.

2.3.4 Discharges with Oxygen and Nitrogen

The reforming of hydrocarbons often occurs in gas mixtures that contain O_2 and N_2 species, such as the partial oxidation of CH_4 with air. In these mixtures, the interaction of N_2 and O_2 in the discharge leads to changes in the breakdown and discharge dynamics. Molecular nitrogen emits UV photons when it returns to ground from an excited state, which results in the photoionization of neutral species in the vicinity. This is especially important for O_2 , as computationally investigated by Naidis for CH_4 —air mixtures [61]. The additional available electrons in the discharge gap sustain the discharge at lower applied voltages, resulting in lower breakdown voltage thresholds. Moreover, the increased electron density produces an increase in space-charge near the streamer head. This slows the streamer propagation speed, allowing higher applied voltages before triggering the streamer-to-spark transition.

On the contrary, without N_2 , the presence of a strong electronegative gas such as O_2 results in electron attachment and the production of negative ions, increasing the rate at which electrons are removed from the system. With fewer electrons, a higher voltage is needed to sustain the discharge, resulting in higher breakdown voltage thresholds. Also, without a space-charge near the streamer head, the electric field is higher, increasing the streamer propagation speed. This results in a streamer-to-spark transition at lower voltages.

The effect of N_2 and O_2 on the breakdown characteristics of the discharge and streamer propagation is observed and qualitatively characterized in Chapter 5.

2.4 Plasma-assisted Fuel Reforming

A plasma discharge in a chemical process produces reactions through excitation, dissociation, or ionization collisions. The efficiencies and the rates at which these collisions happen depend on the electron density, plasma temperature and the reduced electric field of the discharge [15]. For methane decomposition using plasma processes with no catalysts, rotational and vibrational excitations are considered to have no conversion capabilities, because of their short lifespan and low energy. Since most hydrocarbons have bonding energies between 3 and 6 eV, it is clear that molecular excitation, which is typically less than 2 eV, does not result in changes in chemical composition [18]. In this case, electron-impact dissociations are important and act as the initiation of methane dehydrogenation [62].

In reactive gas mixtures, such as those used for partial oxidation reforming, excited species and metastables like oxygen singlet [63, 64] can contribute to the reforming process, as these have lower activation energies when reacting among themselves or with other species in the discharge. Additionally, carbon dioxide requires less energy to dissociate through vibrational excitation, meaning that higher efficiencies are achievable when compared to thermal dissociation [34, 35, 65]. The next subsections present in more detail the state of the art in plasma-assisted methane reforming.

2.4.1 Thermal Plasma Reformers

Thermal plasmas are mainly produced by arc discharges, in which the electron, vibrational, rotational and translational temperatures are in thermal equilibrium. The plasmas produced are continuous and uniform, with high energy content, electron densities, and temperatures exceeding 2000 °C [66], resulting in a very highly reactive media [67, 66]. Consequently, chemical reactions in fuel reformers are enhanced both by high temperature processes and by the presence of highly reactive species [16]. However, a major disadvantage at these operating conditions is particle bombardment which causes electrode erosion. These collisions are wasted energy, effectively lowering the efficiency. Early thermal plasma reforming technology, which relied upon DC torch plasma reactors, yielded close to 70% of hydrogen production consuming 250 MJ for methane pyrolysis, and 100 MJ per kg of H₂ for a combination of steam reforming and partial oxidation [66]. Work on thermal plasmas for dry reforming showed up to 90% methane conversion and an energy efficiency of 48% when using a single-anode plasma jet, where the reactive mixture is not in contact with the discharge [68, 69]. When the reforming feedstock is passed through the discharge, methane conversion decreased while energy efficiency increased, resulting in 79% and 57% respectively [70]. The performance of these reactors is remarkable, but most of the energy is wasted as gas heating, which in some cases can result in systems with lower efficiencies than thermal catalytic reactors [21]. Present efforts focus on non-thermal discharges, which can produce pools of highly reactive species at much lower temperatures.

2.4.2 Non-thermal Plasma Reformers

Non-thermal plasmas are outside of thermal equilibrium and, in the case of molecular gases, these plasmas have higher electron (T_e) and vibrational temperatures (T_v) than their

rotational (T_r) and translational temperatures (T_{gas}) . It can generally be assumed that the inequality $T_e > T_v > T_r$ with $T_r \approx T_{gas}$ is applicable [71]. Non-thermal plasma sources are attractive for hydrocarbon processing as they enable chemical reactions at low temperatures and low power by producing highly reactive species through electron collisions.

Vibrationally excited species are key for fuel reforming reactions at low temperatures in non-thermal plasmas. For instance, vibrational excitation can lead to molecular dissociation through a process called ladder-climbing, which requires less energy than thermal dissociation [34, 35, 65]. Moreover, vibrationally excited CH_4 has a higher probability to dissociate by chemisorption on transition metal catalysts [72, 73]. In dry reforming, the more efficient dissociation of CO_2 means more O_2 molecules become available to oxidize CH_4 .

Electronically excited species also contribute to the low-temperature reforming of reactive mixtures. For oxidative reactions with air, electronically excited N₂ is an important precursor to the formation of electronically excited O₂ species. Electronically excited N₂ is produced via electron impact, and occurs from ground state or other metastable states. After being formed, these excited states proceed to undergo collisional quenching with ground state O₂ producing O(³P), O(¹D), O₂(a¹ Δ_g), and O₂(b¹ Σ_g^+) [74]. The singlet states of oxygen O₂(a¹ Δ_g) and O₂(b¹ Σ_g^+) have relatively low energies and can then be produced in large numbers. Reaction rates of oxidizing reactions such as flames are increased when O₂(a¹ Δ_g) is present in the fuel-air mixture [75]. This occurs mainly as a consequence of lower activation energies when compared to ground state O₂. For fuel reforming, a key reaction is the dehydrogenation of methane. In partial oxidation this occurs as shown in Equation 2.13:

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$
 (2.13)

The previous reaction requires an activation energy of 29529 kJ/kmol. However if

2.4 Plasma-assisted Fuel Reforming

 $O_2(a^1\Delta_g)$ is used instead of ground state O_2 , the required activation energy is lowered to 18262 kJ/kmol [75]. This illustrates the capabilities of non-thermal discharges to enhance the kinetics in oxidative mixtures by populating electronically excited states of N_2 and O_2 .

Common non-thermal plasma sources for fuel reforming are: gliding arcs [76, 27, 77, 78, 79, 80, 81, 82], dielectric barrier discharges (DBD) [55, 83, 84, 85, 86], corona [87, 33, 88, 89, 90] and spark discharges [91, 92, 93, 94, 95, 30, 96].

Gliding arc discharges

Gliding arc discharges are nonstationary and move in between two diverging electrodes. A gas flow, or a magnetic field, may move the discharge in the diverging direction of the electrodes, causing a stretch and an increase in voltage, decreasing the current and cooling down the gas. As a result, the initial thermal arc transits to a non-equilibrium plasma very fast [76]. The voltage increases until the power supply is unable to cope with the demand and the arc extinguishes [15, 27]. These discharges are also known as "warm discharges," as their gas temperature exceeds 1000 °C while remaining in thermal disequilibrium [77, 78]. The higher energy content is attractive for chemical processing, since endothermic reactions can use up to 80 % of the energy provided by the arc [76].

Figure 2.8 shows multiple methane conversion results found in literature from experiments using gliding arc discharges, illustrating the typical performance of these reactors. The highest conversion is obtained in a gliding arc reactor using methane-nitrogen feedstocks and an average power of 224 W. In this study, different methane-to-nitrogen ratios and flow rates are explored, recommending for maximum conversion efficiency a methane-to-nitrogen ratio between 0.1 - 0.4 and a feed flow rate of 8 L/min [79]. The effect of inlet gas composition is investigated by Indarto et al. [80], showing that for their setup, the maximum conversion and hydrogen selectivity are achieved when methane is at 10% and argon or helium are at

2.4 Plasma-assisted Fuel Reforming

90%. Hu et al. [81] finds similar results, suggesting that the increased conversion is given by the Argon metastables, which enhance electron impact reactions. Other studies not included in Figure 2.8, demonstrate the capabilities of low power and compact gliding arc reformers. Results from Ahmar et al. [82] show a 60% methane conversion efficiency with 10% hydrogen yield for a maximum power of 75 W in a compact reactor. Their findings suggest a potential application for gliding arcs as on-board reformers.



Figure 2.8: Methane conversion in gliding arcs. Data from Indarto [80], Hu [81], Zhang [79] and Yuhan [97].

Dielectric barrier discharges

A DBD occurs when an alternating voltage, capable of igniting the discharge, is applied between two electrodes, where one or both are covered behind an insulating material. The dielectric prevents the thermalization of the discharge even at high pressures [16, 15], and allows the formation of multiple filamentary micro-discharges in the streamer regime [55]. In fact, DBDs are of specific interest to chemical processing applications like fuel reforming, as these discharges are capable of producing non-thermal plasmas at atmospheric pressure [16, 55]. Additionally, the scalability and ease of operation are the main advantages of this technology [83].

Preliminary work conducted as part of this thesis focused on using DBDs to show the capabilities of streamer-like discharges for methane decomposition. The reactor consists of a central electrode made of a stainless steel rod of 12.7 mm in diameter and 10 mm in length, placed coaxially inside a quartz tube. The gap between the quartz tube wall and the central electrode is of 1.15 mm, and is where methane flows at a rate of 80 mL/min. The discharge is driven by a 12 kV peak-to-peak and 20 kHz power supply (Information Unlimited, PVM500-1000), which powers the central electrode. An external stainless steel mesh that covers the entire length of the reactor is the ground. Figure 2.9 shows a digital photograph of the DBD setup. Gas composition is analyzed using an online gas chromatograph (Varian, CP-4900 Micro-GC) equipped with a thermal conductivity detector (TCD).



Figure 2.9: Digital photograph of a DBD producing a methane plasma for preliminary studies in methane pyrolysis.

Figure 2.10 shows multiple experimental measurements of the conversion efficiency in

2.4 Plasma-assisted Fuel Reforming



Figure 2.10: Methane conversion in DBDs. Data from Xu [84], B. Wang [98], Q. Wang [99], Nozaki [100] and Li [33].

DBDs, including the preliminary results of this work. It is clear that these discharges require higher specific energy inputs to achieve similar conversion efficiencies when compared to gliding arcs. Conversion efficiency in DBDs increase with increasing residence time [84, 99] and discharge input power [85]. However studies from Wang et al. [99], show that for dry reforming driven by a DBD with an input power of 87.8 W, the reaction reaches a balanced state when the residence time rises to approximately 2 s. After, the conversion efficiency does not improve significantly. Li et al. [33] compared the performance of an AC driven and a pulsed DBD discharge. Their results show that both have similar conversion efficiencies but the pulsed DBD required less energy to operate, making it the more efficient technology. In terms of frequency, Xu and Tu [84] found that the AC wave frequency has only a weak effect on the conversion efficiency. Conversely, in pulsed power DBDs, Khalifeh et al. [101] found that pulsing frequency has a strong effect on the conversion abilities. Moreover, studies with variable pulse duration found that delivering more and shorter pulses results in higher decomposition rate [86]. DBDs produce a large density of vibrationally excited methane, which is ideal for

catalytic applications [55]. There are a large number of studies done with plasma catalysis using DBDs [23, 102, 103, 25, 55], but this is out of the scope of this dissertation.

Corona discharges

Corona discharges are homogeneous discharges that may occur at atmospheric pressure. They are formed typically on a sharp tip where the small radius results in high electric fields [16]. If the input voltage is raised, the corona discharge can transit to a glow and finally to a spark as explained in previous sections. Corona discharges have highly energetic electrons, while the rest of the gas, including vibrational and rotational modes, stays near room temperature [87]. These conditions favor electron impact reactions, which is what makes these discharges interesting for methane reforming.

Figure 2.11 presents the methane conversion efficiency obtained in four different studies using corona discharges as fuel reformers. The operative range of these discharges appears to be similar to the DBDs. The main difference is their increased acetylene selectivity instead of ethane [33, 88, 89, 90]. The study by Redondo et al. [88], showed that the electrode composition is important for methane conversion, reaching a maximum value of 24 % when the electrode was coated with gold to suppress carbon formation. This was also observed by Zhao et al. [89], who noted a slight catalytic effect when using platinum coated electrodes. In their work, the energy efficiency does not increase with the specific energy input, but instead follows a near quadratic function with a minimum of approximately 10 % at 125 kJ/mol. Using a nanosecond pulses to produce a corona discharge, Ghorbanzadeh et al. [90] shows that delivering more pulses, the conversion of methane is increased, up to a maximum of 13 % at a specific energy input of 721 kJ/mol. Mutaf-Yardimci et al. [87] experimented with a very low power corona (10 W), showing that is possible to achieve up to 16 % methane conversion and approximately 8 % of hydrogen yield by preheating the reactants to 900 °C in a gas recirculation reformer.



Figure 2.11: Methane conversion in corona discharges. Data from Li [33], Redondo [88], Zhao [89] and Ghorbanzadeh [90].

Spark discharges

Spark discharges can be non-thermal plasmas, but a strategy needs to be implemented to prevent thermalization. One of these strategies is using pulses with very short duration and very high voltages. However, spark discharges typically have higher gas temperatures when compared to cold discharges like DBD or corona [30]. For this reason, sparks are considered "warm discharges," similarly to gliding arcs [91].

Methane conversion efficiencies for various experiments using spark discharges for methane reforming are shown in Figure 2.12. These discharges have similar performance when compared to gliding arcs, as the conversion efficiency and the required energy input are on similar ranges. Kado et al. [92] and Moshrefi et al. [93] used DC power sources to produce non-thermal sparks. Their approach to prevent thermalization is different. Kado et al. use the current limiter in the power supply to stop its operation, while Moshrefi et al. use a rotating ground electrode

2.4 Plasma-assisted Fuel Reforming



Figure 2.12: Methane conversion in spark discharges. Data from Kado [92], Moshrefi [93], Wang [94], Li [33], Lotfalipour [30], Yao [95] and Scapinello [96].

which stretches the discharge filament. Both arrive to the conclusion that increasing the interelectrode distance increases methane conversion by allowing a higher applied voltage, rather than increasing the residence time of the gas. Wang and Guan [94] investigated a pulsed spark discharge to produce hydrogen and acetylene. They found that recycling part of the plasma exhaust back into the discharge zone enhanced the reactor, reaching a maximum conversion efficiency of 73 % with 24 kW in discharge power. The best results shown in Figure 2.12 are produced in experiments with nanosecond repetitively-pulsed (NRP) spark discharges. Early studies using NRP spark discharges report a maximum methane conversion of 41 % when operating at a pulsing frequency of 10 kHz [95]. Increasing the frequency further results in higher carbon selectivities, which produced a reduction in their conversion efficiency. Lotfalipour et al. [30] did a complete parametric study of an NRP spark, achieving a maximum of 60 % methane conversion and a 70 % acetylene selectivity. They provide insight into the mechanisms of methane dissociation with a numerical model, highlighting the importance of vibrational excitation. In a similar study with dry reforming, Scapinello et al. [96] reached

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conversion efficiencies of up to 52 %, but found that syngas selectivity decreased with increasing energy input, suggesting that water and solid carbon are competing reactions. They conclude that NRP sparks are among the most efficient discharges for methane reforming.

It is clear that the spark discharge has higher methane conversion efficiency than most of the discharges previously presented. Moreover, the development of high voltage nanosecond pulse generators with short pulse rise-times allows higher applied voltages, potentially further increasing the conversion efficiency. Higher voltages also enable a diffuse glow-like regime, which has not been characterized for this application. The work presented in this thesis covers the characterization of the diffuse and the filamentary regimes. Electrical and spectroscopic measurements are obtained to characterize the discharge breakdown, domain of existence, and quantify the electron number density and the degree of thermal disequilibrium of both the diffuse and the spark regime.

Most of the studies with NRP sparks are done in pure methane. The work presented in the next chapters explores the use of oxidative mixtures such as methane-air or methane-oxygen. These mixtures are studied to identify the role of excited species that otherwise would not contribute in the dehydrogenation of pure methane.

Finally, NRP sparks are known to be at higher temperatures than other non-thermal plasma technologies [30]. However, there has been no study on the effect of gas temperature in the reforming performance of NRP sparks. The work presented in Chapter 6 attempts to answer the question of whether heating the gas or delivering more energy into the discharge is more efficient for reforming.

3

Methodology

This chapter provides the details of the methodology followed to carry out the simulations and experiments described throughout the manuscripts of this thesis. The first section is a detailed description of the considerations and assumptions used in the simulations reported in Chapter 4. Following sections offer a comprehensive description of the details, characteristics and specifications of the instruments, gas discharge assemblies, and electrical and optical diagnostics used in the experimental manuscripts of Chapter 5 and 6.

3.1 Numerical Simulation

Chapter 4 is the only manuscript in this thesis with numerical content rather than experimental. It is a proof of concept that uses simple modelling techniques to reach an important conclusion that paves the way for the experimental work developed later in this thesis. The next subsections present in detail the algorithms, assumptions and models used to calculate the reactivity enhancement due to the addition of syngas to the fuel streams in gas turbine engines.

3.1.1 Thermochemical Mechanisms

Two thermochemical mechanisms are used in the simulations described in Chapter 4: GRI-Mech (GRI) 3.0 [104] and Li et al. mechanism [105]. GRI was developed to model natural gas combustion and it is a tool commonly used in industry. It consists of 325 reactions among 53 species, with reaction rates extensively validated against ignition delay times, laminar flame speeds, and species concentrations using shock tube experiments, twin-counter flow flames, and other reactors [104]. For this work, the laminar flame speed validation against CH_4 -air and $CO-H_2$ -air experiments as well as the ignition delay time validation against experiments with H_2-O_2-Ar , $H_2-O_2-CO-Ar$ and several CH_4 mixtures are of specific interest.

The second mechanism, developed by Li et al. [105], is based on a CH_3OH oxidation mechanism developed by Held and Dyer [106, 107]. It consists of 84 reactions among 18 species. It has substantial validation of its sub-mechanisms against experiments with H_2 , CO and CH_2O . Although the mechanism is not as widely used as the GRI, its validation against H_2 makes it important for this work. The mechanism is developed with special care in reactions involving H_2 , and becomes important when predicting the effect of mixing syngas, produced in reforming reactions, with fuels as an additive.

3.1.2 Fuel Reformer

The fuel reformer modeled in Chapter 4 is a simple reactor that assumes thermochemical equilibrium. First, a gas mixture with a certain composition is injected into the reformer with a certain input temperature. The composition and temperature depend on the source of the gas. Figure 3.1 shows the algorithm used to solve the composition and temperature for each type of reforming concept. For biogas partial oxidation (BPOX), the mixture is biogas and air at 300 K, with an equivalence ϕ of 3. The value of ϕ is the result of an optimization to produce the highest

3.1 Numerical Simulation

amount of H_2 possible. For exhaust gas recirculation and reheating reformer (EGR³), CH₄ is mixed with the exhaust gases of a gas turbine engine, which contain a fraction of O₂. A similar optimization is done as with BPOX, however the ratio between the injected CH₄ and the exhaust gases is not constant and it must be analyzed case by case. After setting the reformer input characteristics, the equilibrium composition and temperature of the mixture are calculated using GRI as the thermochemical mechanism. With this method, reaction rates, intermediates and reaction times are ignored for simplicity, as the reformer is to be characterized experimentally in later chapters.



Figure 3.1: A schematic of the algorithm used to model the fuel reformer.

3.1.3 Gas Turbine Engine

Figure 3.2 shows the algorithm used to model the gas turbine engine. Air and fuel are first isentropically compressed to 35 atm to model the compressor and the injector respectively. It is important to note that the fuel is already mixed with a certain amount of syngas produced from the reformer previously described. The amount of syngas is in fact, the independent variable for the study in Chapter 4. The increase in pressure brings an increase in temperature, which depends on the composition of the fuel and air mixture. Following compression, the fuel and air burn in the combustion chamber and the ratio between fuel and air is controlled to maintain a constant adiabatic flame temperature of 1800 K.

3.2 Instrumentation



Figure 3.2: A schematic of the algorithm used to model the gas turbine engine.

The combustor is modeled in three different ways: An equilibrium solver that determines the adiabatic flame temperature and the exhaust gas composition, a 1-D laminar flame to obtain the laminar flame speed, and a 0-D adiabatic reactor to get the ignition delay times of the fuelair mixtures. The first is similar to the reformer model and is used to reduce the computational time taken to solve a 1-D flame during the multiple iterations to get the target flame temperature. Once the target is reached, the 1-D flame model and the 0-D reactor are processed. The obtained reaction products are isentropically expanded and mixed with CH_4 in the EGR³ case.

3.2 Instrumentation

All the experiments described in later chapters extensively use the instruments detailed in this section. Flow is controlled using Brooks mass flow controllers interfaced with a custombuilt Arduino UNO acquisition card, electrical measurements are taken using high-voltage and current probes connected to digital oscilloscopes, optical diagnostics use a set of lenses, filters and mirrors to focus light into an intensity and wavelength-calibrated spectrometer, and gaseous products are analyzed using a gas chromatograph equipped with a thermal conductivity detector.

3.2 Instrumentation

3.2.1 Flow Control

Gas flows are controlled using mass flow controllers (Brooks, 5850E) in conjunction with needle valves at the experimental assembly. The electromagnetic noise produced by the pulsed power generators is capable of timing out digital communications, stopping the flow momentarily and changing the conditions of the plasma. To prevent this, the mass flow controllers are used in analog communications mode and set to open by keeping the valve voltage at constant 5 V. This way, even under a time-out event the flow is not interrupted, and mass flow controllers act as mass flow readers. Flow-rate is set by the needle valves at the inlet of the experimental assembly.

Analog communications with a computer is not straightforward, and a robust device is needed to maintain communications with the flow controllers even when a time out event occurs. A simple solution are DIY Arduino boards and the myriad of attachments available. For the experiments in this thesis, an Arduino UNO is used as the main communications board with an Adafruit ADS1115 16-bit ADC to read the analog voltage from the mass flow controllers.

3.2.2 Electrical Diagnostics

The electrical characteristics of the discharge are continuously being monitored using different types of voltage and current probes. With these probes, the voltage and current at different points in the circuit or discharge assembly can be measured. The measurements obtained are used to calculate the instantaneous power and energy delivered per pulse to the discharge. These measurements also allow the identification and characterization of the regime at which the discharge is being set. The following sub-sections detail the characteristics of these probes.

Probes

Measuring voltage and current waveforms provides information for the characterization of the pulse generator and plasma source. Depending on the voltage waveform characteristics, the appropriate voltage probe is chosen. Table 3.1 shows the specifications of the two Tektronix passive and grounded voltage probes used in the experimental studies. Probe P2200 is for low to intermediate voltages, used primarily in the characterization of voltages in the driving circuit and DC power supply. Probe P6015A is for high voltages, used in the diagnostic of the pulse generator and to monitor the applied voltage into the discharge cell.

Model	P2200	P6015A
Attenuation	10:1 ±2 %	1000:1 ±3 %
Peak pulse voltage (V)	670 <1 s pulse width	$40 \times 10^3 < 100 \mathrm{ms}$ pulse width
Maximum Bandwidth (MHz)	DC - 200	DC - 75
System Input Resistance (M Ω)	$10 \pm 3\%$ at DC	$100\pm2\%$
System Input Capacitance (pF)	13 - 17	≼3
System Rise Time (ns)	<2.2	<4.7

Table 3.1: Voltage probe specifications per manufacturer

The various probes used for current measurement are all very similar, with the main difference being their usable rise time. Table 3.2 shows the specifications of the two current probes used in the experiments. Both are wideband current monitors manufactured by Pearson Electronics. Probe 110A is used for experiments using a pulse generator that produces pulses with a duration greater than 100 ns. These typically had rise times greater than 20 ns, which made probe 110A adequate. However, experiments with faster pulse generators requires a lower usable rise time, and probe 6585 provides the necessary specifications. It is also recommended for fast pulse rise times, that a 50 Ω terminator is used between the cable and the oscilloscope. For experiments reported in Chapter 6, probe model 6585 is used with a 50 Ω terminator feedthrough (Max power: 1 W, max bandwidth: 1 GHz) from Picotech

3.2 Instrumentation

(https://www.picotech.com/).

Model	110A	6585
Sensitivity (V/A)	0.1 +1/-0 %	0.5 ±1 %
Output Resistance (Ω)	50	50
Maximum Current (A)	10×10^3 (Peak), 65 (RMS)	500 (Peak), 10 (RMS)
Usable Rise Time (ns)	20	1.5
Frequency 3dB cut-off (Hz)	$1 - 20 \times 10^{6}$	$400 - 200 \times 10^{6}$

Table 3.2: Current probe specifications per manufacturer

Oscilloscope

A Tektronix model TDS3054B is the oscilloscope used for electrical diagnostics throughout the thesis. Table 3.3 shows the specifications as provided by Tektronix. The obtained waveforms are acquired by the oscilloscope and transferred to the computer using a GPIB-USB cable (National Instruments, 188417D-01). A script written in MATLAB[®] communicates with the instrument using drivers provided by Mathworks[®], and saves the data in the computer for further processing.

Model	TDS3054B
Bandwidth (MHz)	500
Sample Rate on Each Channel (GS/s)	5
Maximum Record Length	10 K points
Vertical Sensitivity (V/div)	1×10^{-3} - 10
Time Base Range (s)	1×10^{-9} - 10

 Table 3.3: Oscilloscope specifications per manufacturer

3.2.3 Optical Diagnostics

Optical emission spectroscopy (OES) is the technique used to optically characterize the plasmas in this thesis. To capture the emitted light from the plasma source, a set of lenses, mirrors and an optical fiber focuses it into a spectrometer. The following sub-sections describe the optical setup, the spectrometer used, and the calibration procedure for the optical system.

Optical Setup

Figure 3.3 is a schematic of the basic optical setup used throughout the experiments. It consists of a pair of plano-convex lenses, a mirror, a high-pass filter ($\lambda > 280$ nm), and an iris. An optical fiber (190 nm < λ < 1100 nm) connects this setup to the entrance slit of the spectrometer (Acton, SP2300i, f = 30 cm) equipped with a CCD camera (Princeton Instruments, PIXIS 256E, 1024 × 256 pixel², with 26 μ m pixel size). Two gratings were used in the experiments described in Chapter 5 and 6. The first is a 1200 gr/mm grating (blazed at 300 nm), which gives the maximum spectral resolution, and is used for temperature and electron number density estimations. The second is a 600 gr/mm grating (blazed at 300 nm), which has less spectral resolution but a larger wavelength range, and is used to measure the relative intensity of different emission bands. The optical setup is mounted on a displacement stage that moves parallel to the axial direction of the reactor, allowing the acquisition of light from the center line of the reaction zone.

The high-pass filter removes lower wavelength emission produced from highly energetic species and prevents OES contamination from second-order reflections on the diffraction grating located inside the spectrometer. This is especially important for experiments with nitrogen and oxygen species, since the NO γ -bands emit in the 190-240 nm range and their second-order diffraction is observed in the 280-480 nm range [58], which falls in the same wavelengths as the

3.2 Instrumentation



Figure 3.3: Schematic of the basic optical setup.

emission bands of interest for this thesis. The iris limits the solid angle of collection, minimizing the aberrations produced by the edge of the lenses. The focal length (f) of each lens determines the size of the volume from which all light is collected in the plasma. The spot-size diameter (δ_{spot}) of this volume is calculated from Equation 3.1:

$$\delta_{\rm spot} = \delta_{\rm f} \frac{f_2}{f_1}.\tag{3.1}$$

In Chapter 5, the characterization of the plasma is limited to the emission near the powered electrode. For this application, the average characteristics of a relatively large volume are required. The light from the plasma is acquired by a lens with a focal length $f_2 = 300 \text{ mm}$ and is focused onto the optical fiber by a lens with a focal length $f_1 = 100 \text{ mm}$. This setup results in a spot-size diameter $\delta_{\text{spot}} = 600 \,\mu\text{m}$. The optical setup focuses at the anode tip, and the acquired spectrum is the result of the integration along the line of sight.

The experiments in Chapter 6 requires the characterized volume to be sufficiently small

to differentiate among different points separated by 200 μ m along the axial centerline. The lenses are interchanged with respect to the setup for Chapter 5 resulting in focal lengths of $f_2 = 100$ mm and $f_1 = 300$ mm. The spot-size diameter is $\delta_{spot} = 66.7 \,\mu$ m for this set of lenses.

Spectrometer Instrumental Function

The spectrometer resolution is the ability of the instrument to distinguish different wavelengths from an incoming ray of light. The resolution depends on the diffraction grating, the slit opening and focal length of the spectrometer. It can be analytically determined, but to reduce any uncertainty in this thesis, it is experimentally obtained by measuring the instrumental function of the spectrometer. Figure 3.4 shows the emission acquired from a He-Ne laser ($\lambda = 636.2$ nm). Since the linewidth of the laser is very thin, on the order of 1 pm, the measured profile represents the instrumental function of the spectrometer. The instrumental function is later used to convolve modeled atomic and molecular emission lines to produce synthetic spectra. Modeled spectra are used to estimate the electron number density, and rotational and vibrational temperatures of nitrogen.

Spectrometer Calibration

To accurately characterize the plasma using OES, the spectrometer needs to be wavelength and intensity calibrated. A Hg-Ar lamp (Oriel Instruments, Model 6035) with well-defined reference points from its atomic transitions, is used to calibrate the spectrometer in wavelength. The software used is WinSpec-32, which has a built-in algorithm for this task. In summary, the spectrometer must first be set at $\lambda = 0$ nm to remove any general offset. Then, the spectrometer is corrected along the available wavelengths in a particular spectrometer window, using the reference points provided by the calibration lamp.



Figure 3.4: Emission from a He-Ne laser used to determine the instrumental function and broadening.

A similar method is used to calibrate the spectrometer in intensity. A halogen lamp (Ocean Optics, DL-2000), with a known emission profile, is placed at the location where the plasma is formed, and the light produced is acquired by the spectrometer after passing through the whole optical setup shown in Figure 3.3. The data from the manufacturer does not have the same array size as the spectrometer. Furthermore, the intensity measurements of the spectrometer depend on many things, from the acquisition time to the optical element transmission function. To compare them, first, a spline fit is passed through the available points. Then, it is assumed that the center pixel of the CCD is the most accurate, and the spline is normalized at this location with respect to the intensity of the measured emission. Figure 3.5 (left) shows this approach and a comparison of the measured intensity and the lamp data provided by the manufacturer. The spline function from the halogen lamp is divided by the experimental measurement of the lamp to produce a transfer function that corrects any measured spectra at the same wavelength range. Figure 3.5 (right) shows the scaling factors of the transfer function that, if multiplied by the measured spectra, returns the emission as provided by the manufacturer.



Figure 3.5: Calibration data vs measured emission from calibration lamp (left), and the transfer function that corrects acquired spectra (right).

3.2.4 Gas Chromatography

Gas chromatography is a simple technique that gives accurate measurements of gas composition. Throughout the thesis, gas chromatography is used to quantify the volumetric fractions of the injected gases and to characterize the composition of reforming products. The available gas chromatograph (GC) (Agilent 6890N) is offline, requiring samples to be transported in gas sample bags (Supelco, Supel-Inert Foil) and injected into it using a 1 mL syringe (Hamilton, 1000 series GASTIGHT). Once injected, the carrier gas (Ar) transports the sample through the column and into the detector.

The GC is equipped with two 10 m capillary columns: A CP-Molsieve 5Å for permanent gases including CH₄, H₂, CO, N₂, O₂, and a PoraBOND Q for CO₂. The CP-Molsieve 5Å column strongly absorbs CO₂, requiring high temperatures to evaporate it from the column, which ultimately damages it. To solve this problem, a pneumatic valve isolates the CP-Molsieve 5Å column while CO₂ passes through to the detector, preventing contamination

3.3 High-Voltage Pulse Generators

and the need to bake the column often. These columns retain each gas for a determined time depending on the column and injector temperature, and the carrier gas pressure and flow settings. These settings are chosen to allow the sample to be processed within a reasonable time, and to have the detected peaks within the linear response region and fully separated from one another. Once the gas leaves the column, it reaches the thermal conductivity detector (TCD) of the GC. The TCD is basically a heated resistor that changes its resistance value depending on its temperature, which depends on the thermal conductivity of the surrounding gas. Its baseline signal is given by the carrier gas and it will change as other components reach the filament. The main advantage of this technique is that the detector has a very broad range of gases that are measurable, including the gases of interest in this thesis.

Figure 3.6 shows a typical chromatogram acquired after injecting 1 mL of a calibration gas with 15 % CO₂, H₂, CH₄ and CO, and 40 % Ar. Since Ar is the carrier gas, no peak for Ar is observed. The rest are shown at different retention times, with CO₂ appearing while the CP-Molsieve 5Å column is isolated. Once the chromatogram is obtained, the peaks are integrated to obtain the area under the curve. The area under a peak scales linearly with the volume of gas injected. After injecting several different amounts of each gas, a first order calibration curve can be obtained. The calibration curve can then be used to determine the volumetric composition of the injected gas sample.

3.3 High-Voltage Pulse Generators

Two different high-voltage pulse generators with different circuit architectures are used in the experimental studies of this thesis. The first uses magnetic pulse compression to generate pulses of up to 40 kV with a duration of 200 ns at a repetition frequency of up to 7 kHz [108]. The second is the latest generation of pulse generators developed in the Plasma Processing



Figure 3.6: A Chromatography signal from the injection of 1 mL of calibration gas with 15 % CO_2 , H_2 , CH_4 and CO, and 40 % Ar.

Laboratory. It is a diode opening switch, that uses a similar driving architecture as other pulse generators [29, 108] with the addition of diode stacks to reduce the pulse duration and increase the pulse amplitude. It is capable of producing pulses of up to 15 kV and 40 ns in duration at a repetition frequency of up to 10 kHz. The next sub-sections provide the details and characteristics of the pulse generators used in the chapters ahead.

3.3.1 Magnetic Pulse Compression Pulse Generator

Figure 3.7 shows the schematic of the magnetic pulse compressor used for the experiments in Chapter 4. To produce a pulse, a power supply (PS) (Sorensen, DCR 600-4.5B) with a capacitor C_0 (10 μ F) at V_{PS} charges C_1 (3.7 μ F) through L_0 (560 μ H) during the OFF-time of the transistors (T_1 to T_6). The transistors $T_1 - T_6$ are IGBTs (IXYS, IXYH60N90C3) with a maximum 900 V hold-OFF voltage between the collector and the emitter. IGBTs are driven by the amplified signal of an external trigger generator (Berkeley Nucleonics, BNC 565). During the ON-time, C_1 is discharged through the high-current diode D_0 (Fairchild Semiconductor, RURG80100), producing a current to flow through the primary windings of transformer PT_1 .

3.3 High-Voltage Pulse Generators

Pulse transformer PT_1 has a stack of four nanocrystalline cores (Hitachi Metals, FT3KM F6045G) with a 1:50 ratio between the primary and the secondary windings. Current flow on the primary side induces a current on the secondary which charges capacitor C_2 (1.1 nF). After reaching a full charge, C_2 discharges through the primary windings of PT_2 , which is made of a stack of four nanocrystalline cores (Hitachi Metals, FT3KM F4535G) with a 7.5:12 stepup ratio. The induced current on the secondary side of PT_2 charges C_3 (500 pF). The voltage pulse at this point has a duration of 2.5 μ s and an amplitude of 10 kV for a V_{PS} of 200 V at 1 kHz repetition rate. Once C_3 is charged, the magnetic switch MS_1 saturates and cascades the energy of C_3 through branches a and b, charging capacitors C_{4a} and C_{4b} (470 pF). Similarly, MS_2 saturates and cascades the energy to C_{5a} and C_{5b} (235 pF). The magnetic switches MS_1 and MS_2 are made of stacks of three single cores (Hitachi Metals, MP3210M4AS) with two parallel windings in the same direction of 20 turns each. At this point, the voltage at each branch is stepped up with transformers PT_{3a} and PT_{3b} , made of single cores (Hitachi Metals, MP3210M4AS) with a step-up ratio of 10:33. The added contribution from PT_{3a} and PT_{3b} results in a voltage pulse of 29 kV with a full width at half maximum (FWHM) of 90 ns at 1 kHz repetition rate for a $V_{\rm PS}$ of 200 V. The voltage pulse amplitude and duration depend on the input voltage. This pulser is capable of producing pulses of more than 40 kV and possibly lower pulse durations; however, these values exceeded the capability of the available voltage probes.



Figure 3.7: Circuit diagram of the magnetic pulse compressor adapted from [108].

3.3.2 Diode Opening Switch Pulse Generator

Figure 3.8 shows the schematic of the latest version of the diode opening switch developed in-house. The primary block is similar to the magnetic pulse compressor, but with different components. The transistors $T_1 - T_6$ are a different model of IGBTs (IXYS, IXGH50N90B2D1) with the same maximum hold-OFF voltage. PS represents two power supplies in series (Sorensen, DCR 600-4.5B and Hewlett Packard, 6448B), capable of reaching up to 1.2 kV DC. Capacitor $C_{\rm f}$ (2.7 μ F) and $R_{\rm f}$ (250 Ω) produce a filtering effect that protects the DC source from voltage fluctuations and store energy that is delivered to C_0 (40 nF) through diode D_0 (Fairchild Semiconductor, RURG80100). Diode D_1 is the same as D_0 and allows current to circulate back to C_0 . The capacitor then discharges through the primary windings of the pulse transformer PT. The latter is composed of a single core (Hitachi Metals, MP3210M4AS) with a step-up ratio of 1:10 and winded up to produce a negative voltage at the secondary of the transformer. The current induced in the secondary windings of PT charges C_1 (470 pF). As C_1 is discharged, the current passes freely through the diode bank $D_{\rm B}$, composed of multiple diodes (Vishay Electronics, MURS360-E3/9AT) in series and parallel. When all the minority carriers in the PN junction of the diode are extinguished, the current flowing through $D_{\rm B}$ is interrupted, and the remainder of the energy in the L_1 is delivered to the load. This accumulates charges rapidly which causes a rapid increase in potential in a very short time. The effect is similar to water hammering in pipelines, with pressure being an analogy to voltage. Inductor $L_{\rm S}$ acts as a large resistor until it saturates and short circuits to ground. This cuts the pulse duration and reduces oscillations in the produced waveform. This pulser is capable of reaching 15 kV with pulse durations of 40 ns and rise times of 20 ns at repetition frequencies of 10 kHz. It is limited by the DC PS, and the IGBTs, which can have up to 900 V between the collector and the emitter.



Figure 3.8: Circuit diagram of the diode opening switch.

3.4 Experiment Design

The basic electrode setup used in the experimental assemblies is a pin-to-plane configuration. The high-voltage pulse generator is connected to the pin electrode, making it the anode. Conversely, the plane is connected to the ground, making it the cathode. The pin is a 304 stainless steel 22 gauge (0.016" ID, 0.028" OD) needle, which serves both as an electrode and as the gas delivery system. With this configuration, the plasma is formed at the outlet of the needle, which is also the only path the gas can take out to the reaction zone. This way, the gas is directed towards the volume where the plasma is formed, and the amount of gas treated by the discharge is maximized. Additionally, the needle is sharpened at the tip, providing a localized increase in the electric field to facilitate the ignition of the discharge. The gas is fed to the needle through the gas lines described in Subsection 3.2.1. The reactor is fully enclosed in a GE type 214[®] quartz tube to isolate the reacting gases from the atmosphere and allow optical accessibility. Quartz is a dielectric material, with a poor thermal conductivity and capable of withstanding temperatures in excess of 1000 K. It is optically transparent in the UV-visible range. Figure 3.9 shows a schematic of the basic experimental configuration.



Figure 3.9: Schematic of the basic pin-to-plane configuration (left) and the quartz tube transmittivity (right).

3.4.1 Adjustable Ground Assembly

The assembly used in Chapter 5 is designed to have a movable ground to allow the control of the applied voltage, assuming that the breakdown characteristics of the discharge cell remain the same. The ground mesh is 19.05 mm in diameter with a density of 100 x 100 wires per inch, and is welded to a stainless steel tube that holds it perpendicular to the pin electrode. The tube is able to slide along the axial direction, changing the distance between the tip of the needle and the ground. The mechanism that moves the ground allows the variation of the inter-electrode distance in increments of 1.5 mm. The anode assembly is embedded in alumina ceramic. The ceramic acts as a thermal and electrical insulator, effectively isolating everything except for the tip of the needle that is exposed to the reaction zone.

Chapter 5 is a study of the different discharge regimes, one of which produces a volumetric plasma. By approximating the radial size of the plasma from previous work [108], the reactor inside diameter (ID) is chosen to be 20 mm to prevent interactions between the discharge and the walls. In this regard, a protruding piece of ceramic is added to hold the quartz tube in place from the inside and center it with respect to the needle. Sealing between the quartz tube and the atmosphere is ensured with conventional rubber o-rings. Figure 3.10 is a cross-section of a 3D



CAD model of the reactor showing the details of the experimental assembly used.

Figure 3.10: CAD model of the adjustable ground assembly.

3.4.2 High Temperature Assembly

The assembly for Chapter 6 is similar to the previous one. Instead of a movable plane, the ground of this assembly is fixed and is made of brass. Brass is made out of copper and zinc, which have emission lines in the visible range, and are a good indicator of electrode ablation. Moreover, brass has good thermal conductivity, which allows for temperature measurements to be taken at the ground electrode. In this case, there is no mesh, only a hole with a diameter of 0.7 mm centered in the ground plane from where gases exit the reactor. The experiments in Chapter 6 are expected to be mostly in the filamentary regime, which is composed of thin plasma filaments. To reduce the amount of dead volume, the ID of the reactor is reduced to 4 mm. Figure 3.11 shows the cross-section of a 3D CAD model of the high temperature assembly.

Chapter 6 deals with different energy inputs, one of which is delivered by preheating the reactants. Preheating far away from the needle proved ineffective for the flow rates used as the



Figure 3.11: CAD model of the high temperature assembly.

gas would arrive at room temperature to the reaction zone, regardless of the thermal insulation used for the whole assembly. The only way to set the temperature of the reactants is to heat them in-situ, at the needle directly. This is not straightforward as high voltages add a degree to the complexity of the system. Electrical heaters are one of the easiest solutions to implement when it comes to flow heating, as they are compact and heating controls are well-developed and accurate. However, the insulation that these devices typically have is not meant for highvoltages. Moreover, electrical heater controls rely on thermocouples as input in their control loop, which do not work near pulsed-power applications. Adding insulation to these devices, for instance layers of ceramic coating, reduces their heating efficacy and the control accuracy since a larger temperature gradient is formed as the insulation layer grows. Also, even with thick insulating layers, some gas trapped in between can be ionized forming micro dielectric barrier discharges that could damage the heater and be dangerous to the operator. For these reasons, the assembly used an alternative approach: reactants are heated using a methane-air flame.

Methane flames can burn in excess of 2000 K delivering up to 50 MJ per kg of methane

assuming complete combustion. Methane burners can be simple devices and do not require electrical components. Flames are relatively unaffected by the electric field around the needle and can steadily provide heat to the reactants. For this particular assembly, methane and air are premixed and burned at the outlet of a 0.25" alumina tube. The amount of reactant heating is controlled both by the flame equivalence ratio and methane flow. To allow heating by the flame, the anode in this case is exposed and not insulated, with the flame sitting directly below the stainless steel needle. The flame allowed preheating of the reactants from 400 to 700 K, with a maximum variation of 5 K.

4

Reformed Gas for Reactivity Enhancement

4.1 Preface

This chapter presents the results of studying the addition of syngas produced by reforming exhaust gas and biogas into the fuel inlet stream of a gas turbine at typical operating conditions. The work was planned and executed by P. D. G. Maqueo. P. Versailles provided guidance and support using CANTERA[®] and CHEMKIN[®]. G. Bourque provided guidance on gas turbine engine operation and ran simulations to validate results. Supervision of the research, and reviewing of the manuscript was done by J. M. Bergthorson. The citation for this chapter is:

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4.1 Preface

A gas turbine engine and a reformer were numerically modeled in CANTERA[®] and CHEMKIN[®] to calculate the effect of syngas in the laminar flame speed and ignition delay time of the fuel-air mixture. These models used the Li et al. [105] and GRI-Mech [104] thermochemical mechanisms to calculate gas composition and temperature, laminar flame speed, and the ignition delay time. Fuel reforming composition and temperature were modeled assuming thermochemical equilibrium is reached. For the gas-turbine-engine model, three different reactors were considered: a thermochemical equilibrium solver to determine the product composition, a 1-D laminar flame to calculate the laminar flame speed, and a 0-D reactor to determine the ignition delay time. To decouple the contribution from temperature in the enhancement of reactivity, the adiabatic flame temperature was kept constant at 1800 K by controlling the equivalence ratio of the mixture. Also, to separate out thermal and chemical effects, the model considers a second case in which the reformed gas loses all heat and cools down to 300 K before mixing with the fuel.

It was found that syngas increases the laminar flame speed and reduces the ignition delay times when mixed with methane or biogas previous to the combustor, showing an enhancement in the reactivity of the mixture. It was observed that this effect was present even if the mixture was cooled down to 300 K, showing that chemistry alone can increase reactivity. Additionally, it was found that the exhaust gases of gas turbine engines can be used to drive reforming reactions, allowing the partial reuse of heat that, otherwise, would be lost.

A Numerical Study on The Reactivity of Biogas/Reformed-Gas/Air and Methane/Reformed-Gas/Air Mixtures at Gas Turbine Relevant Conditions

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Abstract. This study investigates the increase in methane and biogas flame reactivity enabled by the addition of syngas produced through fuel reforming. To isolate thermodynamic and chemical effects on the reactivity of the mixture, the burner simulations are performed with a constant adiabatic flame temperature of 1800 K. Compositions and temperatures are calculated with the chemical equilibrium solver of CANTERA[®] and the reactivity of the mixture is quantified using the adiabatic, freely-propagating premixed flame, and perfectly-stirred reactors of the CHEMKIN-Pro[®] software package. The results show that the produced syngas has a content of up to 30 % H₂ with a temperature up to 950 K. When added to the fuel, it increases the laminar flame speed while maintaining a burning temperature of 1800 K. Even when cooled to 300 K, the laminar flame speed increases up to 30 % from the baseline of pure biogas. Hence, a system can be developed that controls and improves biogas flame stability under low reactivity conditions by varying the fraction of added syngas to the mixture. This motivates future experimental work on reforming technologies coupled with gas turbine exhausts to validate this numerical work.

4.2 Introduction

Rising energy demand and increasingly stringent air pollution regulations in the world are driving a search for alternative, renewable and clean energy sources. Biogas is a renewable fuel produced by organic decomposition. One of its main components is methane, which acts as the fuel; the other is carbon dioxide which is a diluent that lowers the reactivity and energy density of biogas. Lower reactivities pose a problem for lean premixed gas turbines (GT). As the fuel mixture is made leaner, both, the adiabatic flame temperature and flame speed decrease. The latter is an indicator of the reactivity of a mixture, and it is fundamental in burner design and combustion modeling [109]. If the laminar flame speed is too low, instabilities arise and could eventually lead to blowout. For this reason, low-grade fuels like biogas might not be adequate for operation in lean-premixed mode.

It is possible to extend the flammability limits of a fuel by adding more reactive species such as hydrogen [1, 2, 3]. However, hydrogen gas is not readily available, and it is currently mainly obtained from hydrocarbon reforming [110]. There are three main reforming techniques: steam reforming (SR), dry reforming (DR) and partial oxidation (POX) [111, 14, 112, 113]. The product of these processes is a hydrogen containing gas known as syngas, which is used as a reactivity booster in this study.

Industrially, the most important for hydrogen production is methane steam reforming [110]. It is the endothermic reaction of steam and methane which produces the highest hydrogen to carbon monoxide ratio [111].

Dry reforming (DR) is another endothermic reaction to produce syngas. It is the most interesting one in terms of reducing pollutants, since its two main components are two important greenhouse gases. Also, biogas is a mixture of CH_4 and CO_2 [114] making it a suitable feedstocks for dry reforming [115, 116, 117].

4.2 Introduction

Partial oxidation (POX) is a reforming process that involves exothermic oxidizing reactions. It can be combined with the previous two so the generated heat can be used to feed SR and DR reactions. Furthermore, POX, SR and DR can be equilibrated to have a net zero energy release. This configuration is known as autothermal reforming (AR) [118].

There are other variations of these basic processes, which means that syngas may be produced from a myriad of feedstocks and production methods [18, 119, 120, 121]. This makes syngas an attractive flexible fuel that can be produced from low calorific fuels. In fact, there is extensive literature on syngas reactivity: laminar flame speeds [122, 123, 124, 125, 126, 127, 128] and ignition delay times [129, 130, 131, 132, 128]. Fundamental experimental studies have been conducted investigating the combustion properties of syngas and fixed hydrocarbon-syngas mixtures [133]. A recent paper discusses laminar flame speeds and ignition delay times of real syngas mixtures including fixed hydrocarbon-syngas mixtures [134]. Watson et al. [135] investigated NO formation from biogas-syngas blends and obtained laminar flame speeds for a various fixed hydrocarbon-syngas mixtures. However, to the authors' knowledge there is no study on syngas increasing the reactivity of the fuel-air mixture while keeping a constant flame temperature at gas turbine relevant conditions. This is explored by progressively adding syngas to the fuels, controlling the equivalence ratio of the mixture to keep the same flame temperature and calculating their laminar flame speeds and ignition delay times. Moreover, two reforming technics are studied: biogas partial oxidation and a concept of a reformer coupled to the exhaust of the turbine.

The objective of this study, is to assess if reformed gases can improve the reactivity of low calorific fuels like biogas in a GT without changing the initial pressure and flame temperature in the combustor. The motivation for this work is that such a configuration would allow for greater fuel flexibility at lean premixed conditions. A key parameter used to compare different fuel blends in terms of their heating value is the Wobbe index. It is an index with which the ability

of the fuel system to handle the composition of the fuel can be judged [136]. Although different fuel blends are explored, this study focuses on its laminar flame speeds, an effect which is not captured by the Wobbe index.

The paper first covers the details of the modeling procedure and the reformer settings. Then, results on ignition delay times and laminar flame speeds follow. The paper closes with a discussion on the characteristics of the fuel-syngas mixtures, their reactivity, and specific applications of the proposed concept.

4.3 Methodology

A land-based gas turbine engine represents the basis for the model in this study as depicted in Figure 4.1. Additionally to the traditional engine components, there is a reformer connected to the fuel line prior to the combustor. The reformer model is an infinite time reactor where the mixture is allowed to reach chemical equilibrium. Perfectly-stirred mixtures are assumed at any connection point. To measure the effect of the reformed gas, a fraction of it is added to the fuel. Two cases are analyzed: The first is termed the exhaust gas recirculation, reheating reformer (EGR³) as it consists in recirculating the exhaust gas, reheating it through methane oxidation and reforming it. The second is termed biogas partial oxidation (BPOX) case, which uses a biogas reservoir as the input for the reformer. The biogas used in this study has an equimolar fraction of CH_4 and CO_2 .

The calculations and results presented here are obtained from numerical simulations using various CANTERA[®] and CHEMKIN-Pro[®] packages with GRI-Mech 3.0 [104] and Li et al. [105] thermochemical mechanisms. Gas compositions and temperatures are calculated using the equilibrium package of CANTERA[®] within the reformer and combustion chamber. Reactivity is determined by calculating laminar flame speeds and ignition delay times in



Figure 4.1: Model schematic: (a) biogas partial oxidation (orange line), (b) methane - exhaust gas reforming (blue line)

CHEMKIN-Pro[®]. For all cases laminar flames are simulated using the 1D flame models and the ignition delay times of the mixture are obtained from closed PSR models at constant pressure and internal energy.

4.3.1 Gas Turbine Engine Modeling

The modeled gas turbine engine is based on the Brayton cycle. Air and fuel are compressed isentropically prior to the combustor to reach 35 atm. Air temperature, which is initially at 300 K, increases to 828 K due to compression. Fuel temperature depends on the initial fuel (biogas or methane) and the amount of added reformed gas. The equivalence ratio is varied to keep the post-flame temperature at 1800 K, which is similar to typical gas turbine engines [137]. The consequent fuel-air mixture composition and temperature depend on various parameters: the fuel used (biogas or methane), the amount of reformed gas mixed in with the fuel and the

4.3 Methodology

equivalence ratio.

The first step to determine the parameters of the engine is to define two baselines as cases where the fuel mixture includes no reformed gases. They are the initial reference points for each fuel. The first is methane, which at $\phi = 0.45$ has an adiabatic flame temperature of 1800 K. The second is biogas which requires a $\phi = 0.49$ to achieve the same temperature. The fuel streams are compressed to 35 atm and then mixed with compressed air at 828 K and result in a combustor inlet temperature of 816 and 805 K respectively. These temperatures are similar to typical gas turbine engine conditions as seen in [137, 138]. The obtained baselines serve as a starting point for variations of the parameters of the engine and as a reference for the performance of other mixed fuels.

When adding reformed gas to the fuel mixture, the temperature of the combustor and the composition of the exhaust gas change. The equivalence ratio is the controlling parameter that regulates the temperature to keep it at 1800 K in the combustor. For the BPOX reformer, this is enough to know all the parameters at the combustor inlet. However, the EGR³ reformer case is more complex since the composition of the inlet gas depends on the reformed gas, which depends on the exhaust gas composition, creating an information loop.

The algorithm to solve the information loop in the EGR³ reformer case is a series of iterations depicted in Figure 4.2. The program first sets the combustor composition at the baseline corresponding to the selected initial fuel. Then, the exhaust gas goes into a mixer with methane and becomes the inlet of the reformer. The exact fraction of exhaust gas and methane in the mix is an optimization problem which aims at maximizing the hydrogen content in the reformed gas. The resulting syngas is fed through a valve that controls its ratio with the initial fuel. This is the independent variable and is set from 0 to 100 %.



Figure 4.2: Algorithm used in determining gas compositions, temperatures and optimizing the reformer. Blue lines represent control parameters

4.3.2 Fuel Reformer

Gas turbine engines have an exhaust primarily composed of a mixture of H_2O , CO_2 , O_2 and N_2 . Methane mixed with H_2O and CO_2 enable steam and dry reforming respectively. These two reactions are endothermic and, in typical applications, they require an external heater. However in this case, the exhaust gas coming from the gas turbine is at high temperature and contains energy useful for these reactions that would otherwise be wasted. Another energy input comes from partial oxidation, which is a result of mixing CH_4 with the remaining O_2 from the exhaust. Hence a mix of methane and exhaust gases resulting in POX, SR and DR reactions is presented.

Biogas is used as a fixed feedstock for the BPOX reformer case. Biogas composition is a particularly convenient since it contains the two major components for DR. However, DR needs an energy input, but instead of assuming an external heater, air is flowed in to partially oxidize

4.3 Methodology

biogas. Therefore, a fraction of CH_4 oxidizes, providing energy to the DR reactions. Hence it is a combined POX and DR reactor.

All simulated reformers have a certain amount of oxidative reactions releasing heat. Consequently the output of the reformer is always at a higher temperature than the incoming feedstock mixtures. There are two extremes considered for the reformed gases: An adiabatic reactor where no heat losses occur from the output of the reformer to the combustor inlet, and a complete heat loss case where the reformed gases are cooled down to 300 K. The latter is especially important to assess the chemical reactivity of a mixture as it would be independent of temperature effects.

4.3.3 Reactivity Calculations

The laminar flame speed (S_L) is defined as the speed at which an adiabatic unstretched laminar flame propagates in a uniform fuel-oxidizer mixture [38]. Equation 4.1 shows the laminar flame speed proportionality with respect to the thermal diffusivity (α) and the overall Arrhenius reaction rate evaluated at the adiabatic, post flame temperature ($\dot{\omega}_b$). It is one of the two parameters used in this study to determine the reactivity of the fuel-air mixture.

$$S_{\rm L} \propto \sqrt{\alpha \dot{\omega}_{\rm b}}$$
 (4.1)

Another indicator of the reactivity, a parameter that measure the amount of time a perfect mixture of fuel and oxidizer needs to auto-ignite, is the ignition delay time (τ_{ign}). It is inversely proportional to the overall Arrhenius reaction rate evaluated at the combustor inlet temperature ($\dot{\omega}_{in}$) as seen in Equation 4.2. This is the second parameter used for determining the reactivity of the fuel mixture.

$$au_{
m ign} \propto \frac{1}{\dot{\omega}_{
m in}}$$
(4.2)

In a lean premixed gas turbine engine, premixing of fuel and air takes place before the combustor. If the ignition delay time is lower than the time it takes for the mixture to reach the combustor, then auto-ignition happens. This is particularly disastrous as the components of the engine in the premixer are not designed to sustain high temperatures characteristics of a flame. Prevention of auto-ignition is consequently an upper limit for the reactivity of a mixture.

4.4 Results

Baseline calculations, observed at 0 % syngas in Figure 4.9 and Figure 4.10, result in laminar flame speeds of 13.3 cm/s and 12.2 cm/s and ignition delay times of 1.78 and 2.6 seconds for methane and biogas respectively. These correspond to previously discussed equivalence ratios of $\phi = 0.45$ for methane and $\phi = 0.49$ for biogas to have a flame temperature of 1800 K in the combustor.

To get a maximum increase in reactivity, reformers are optimized to get the highest H_2 content in the syngas produced. EGR³ reformers require optimization for each varying point, since its feedstock depends on the burners characteristics. In contrast, BPOX require only one point.

4.4.1 **Reformer Optimization**

EGR³ Reformer

Initially, in a EGR³ reformer case, the only gases flowing through the reformer are only GT exhaust gases. Then results seen in Figure 4.3 show a temperature increase as methane is



Figure 4.3: EGR 3 Reformer outlet conditions: syngas $\rm H_2$ and CO Content, and gas temperature increase

added and reacts with the remaining O_2 of the exhaust gases. The maximum reformer exhaust temperature (T_{out}) is reached when there is a stoichiometric mixture of CH₄ and the exhaust gases. Also, at this point, results show a maximum CO₂ and H₂O content in the reformed gases, indicating methane combustion. As the mixture is made richer, the temperature decreases. These conditions are marked by an increase in H₂ and CO in the reformed gas. As more methane is added, the mixture approaches an CH₄/O₂ ratio of 2 which is characteristic of POX [113]. At a certain point the optimum is achieved when hydrogen content reaches a maximum at 30% and the reformed gas temperature is close to its minimum. This happens approximately when the molar fraction of the reforming feedstock is 1/4 methane, while the rest is exhaust gases.

BPOX reformer

For a BPOX reformer, the only changing parameter is the amount of air added. Air oxidizes the CH_4 component of biogas and, although it is diluted with CO_2 , the results are similar to pure CH_4 oxidation as seen in Figure 4.4. As the composition of the feedstock is not changing, the



Figure 4.4: BPOX reformer outlet conditions: syngas H_2 and CO Content, and gas temperature increase

optimum point for this reformer is fixed. Similarly to a EGR³ reformer, the optimum is defined as the point where the maximum H₂ content is achieved. This occurs at a ϕ = 3.0 and has a yield of 21 % hydrogen by mole fraction.

4.4.2 Combustor Inlet characteristics

Ideal reformers are assumed where chemical equilibrium is reached and syngas composition varies according to the feedstock used. Once it is mixed with the fuel at the combustor inlet, it results in 4 different mixtures which depend on the reformer and fuel as seen in Figure 4.5. Results show that EGR³ reformers end up producing fuel mixtures with the highest H_2 content for both fuels.

Biogas-syngas blends show a higher inlet temperature than methane-syngas mixtures as seen in Figure 4.6. The reason is that mixtures with a lower heating content require more fuel added into the mixture to achieve the set adiabatic flame temperature of 1800 K. More fuel means more syngas is mixed in, which already comes at a high temperature.



Figure 4.5: Fuel-syngas mixture composition at combustor inlet: a) biogas - EGR³ reformer, b) methane - EGR³ reformer, c) biogas - BPOX reformer and d) methane - BPOX reformer

High inlet temperatures produce high laminar flame speeds and low ignition delay times. These results show a potential problem of having a mixture that is too reactive and achieves auto-ignition in the premixer.

4.4.3 Auto-ignition regime

Increasing the temperature and H_2 content of the fuel could increase the propensity for auto-ignition of the fuel-air mixture in the engine premixer. Therefore, ignition delay times are first calculated using a closed PSR at constant pressure and internal energy. Simulated adiabatic EGR³ reformers produce the most reactive mixtures in this study and consequently have the lowest ignition delay times. If auto-ignition occurs, these mixtures would mark the upper limit at which the reactivity of the mixture can be increased.



Figure 4.6: Combustor inlet temperature $(T_{c-inlet})$

Upon further inspection of the auto-ignition regime simulations, it can be observed that laminar flame speed calculations begin to scale with the domain length. This grid dependant scaling occurs because the flame speed becomes controlled by the low-temperature reactivity of the mixture, ω_{in} , instead of the high-temperature chemistry, ω_{b} . This phenomenon has previously been observed in MILD combustion systems [139]. As a result, reliable flame speeds can only be calculated for mixtures with sufficiently long ignition delay times. A comparison of the ignition delay time and the residence time of the reactants (τ_{res}) upstream to a laminar flame, calculated as the time delay between the inlet of the computational domain and the location of maximum temperature gradient through the flame, show that at a certain point both have the same order of magnitude as seen in Figure 4.7. Any cases with a $\tau_{res} - \tau_{ign} < 0.5 \tau_{ign}$ are considered unreliable and the resulting flame speeds are not presented. This corresponds to a point where $\tau_{ign} < 150$ ms at a mixture of 40 % syngas with the fuel for the adiabatic reformer case.



Figure 4.7: Estimation of auto-ignition regime: a) timescales with respect to syngas content b) definition of timescales

4.4.4 Reactivity of the mixture

Results show that reformers can produce hydrogen containing fuel mixtures with temperatures exceeding 1100 °C. Both increase the reactivity of the gas and consequently lower their ignition delay times. These are presented in Figure 4.8, complementing the lack of reliable laminar flame speed data for the adiabatic GT and reformer case. Initially, biogas reactivity is lower than methane, but this changes after 15-20% of the fuel mixture is syngas. The main reason can be seen in Figure 4.6 and Figure 4.8. Biogas fuel mixtures have higher temperatures, which correspondingly have ignition delay times following opposite tendencies. Plotting the ignition delay time against temperature confirms this in Figure 4.8 and shows that reactivity for the adiabatic case is dominated by temperature effects.

Pure syngas corresponds to the fuel mixture with the highest reactivity. The results on ignition delay times for pure syngas are close to $500 \,\mu$ s which means an increase of up to 3×10^3 times the reaction rate of pure methane-air mixtures. As this mixture is well into the auto-ignition regime, no laminar flame speed calculations were attempted.



Figure 4.8: Ignition delay time for adiabatic case with respect to a) syngas content and b) temperature

Results show a marked increase in the laminar flame speed as fractions of syngas are added to the initial fuel, as seen in Figure 4.9. Having a similar tendency than ignition delay times, it is observed in Figure 4.9 that after 15 % syngas in fuel mixture, temperature effects dominate and the hottest mixture reaches a higher laminar flame speed than the mixture EGR³ produces, which has a higher H_2 content.

To get the chemistry effect on the reactivity, there is a final case considered, where reformed gases are cooled down to 300 K. These are considerably less reactive conditions, that are far from the auto-ignition regime. In Figure 4.10, the effect of adding syngas to the fuel mixture is seen up to 100 %. It shows a clearer distinction between each reformer type since the main difference between mixtures is their H_2 and CO content now that the temperature effect is negligible. The maximum laminar flame speeds are obtained by EGR³ reformers, achieving and increase over the baseline of methane and biogas of 20 % and 30 % respectively. BPOX has a considerably lower increase of 10 % and 20 % for the baseline of methane and biogas.



Figure 4.9: Effect of adding syngas to the fuel stream assuming no heat loss: a) methane, b) biogas

4.5 Discussion

The presented results show, for all cases, an increase in the laminar flame speed and a decrease in the ignition delay time, both which represent an increase in reactivity. Reaction rates are more than 3000 times higher than methane-air mixtures. These results are a product of the combination of the effects of an increased temperature and a more reactive mixture. For the adiabatic case, Figure 4.8 shows that ignition delay time has an exponential dependence on temperature, as expected. This shows that the reaction rate increase is mainly a temperature effect, dominating over any existing hydrogen enhanced chemistry. Moreover, the ignition delay time decreases to a point where it is on the order of magnitude of the residence time in the premixer before the combustor. At this point, it is likely that in a real application auto-ignition occurs.

A more useful indicator of the effects of syngas chemistry on the enhancement of reaction rates is seen when the reformed gases are cooled down to 300 K. Under these conditions, all



Figure 4.10: Effect of adding 300 K syngas to the fuel stream: a) methane, b) biogas GT

blends of fuel and reformer gas enter the combustor at the same temperature. An increase in laminar flame speed is achieved by increasing the fraction of syngas added into the initial fuel line as seen in Figure 4.10. Although not as dramatic as the increase seen in the adiabatic case, it is possible to boost the initial laminar flame speed up to 33 % higher when operating at full syngas.

In a real application, the situation would not be one of the two extremes and would have a combined effect from temperature and chemistry. Furthermore, the GT with a EGR³ reformer can be optimized so reactivity is controlled by either the temperature or by the syngas blend.

Assuming no heat loss, 15% syngas mixed with biogas is enough to surpass the laminar flame speed of pure methane for both mechanisms and fuels. Since in this case reactivity is mostly dependant on temperature, both reformers: EGR³ and BPOX, yield the same result as seen in Figure 4.9 (b). When heat losses are factored in, the reformed syngas composition alters the reactivity. Figure 4.10 (b) shows the laminar flame speed of biogas-syngas mixtures as a function of the amount of syngas in the fuel assuming heat loss. It can be seen that for GRI 3.0 [104] calculations, 55/45 biogas/EGR³ syngas and 45/55 biogas/BPOX syngas

4.6 Conclusions

mixtures, achieve laminar flame speeds similar to pure methane flames. Similarly, a mix of 30% syngas with biogas is needed to reach the laminar flame speed of methane when using Li et al. [105] mechanism. These results show it is feasible to use any of these techniques to increase reactivity of biogas to the point where the laminar flame speed is similar or higher to that of methane.

4.6 Conclusions

The intention of the numerical study presented in this paper is to provide a qualitative assessment of the reactivity improvement by mixing an initial fuel with the products of EGR³ and BPOX reforming. However, given GRI [104] and Li et al. [105] mechanisms are not fully validated for these operating conditions, further laminar flame speed measurements (e.g. combustion bombs [140]) and ignition delay time experiments (e.g. shock tubes [141, 142, 143, 144]) should be performed to confirm the accuracy of these predictions.

Syngas addition to a fuel stream results in an increase in the reactivity at GT conditions. The effect is a combination of an increased temperature, produced by the reforming process, and an improved chemistry through the addition of more reactive H_2 into the mixture. It is shown that, even when heat losses are present, and the temperature of the mixture flowing from the reformer goes down to 300 K, the chemistry effect is strong enough to produce an increase in laminar flame speeds. The effect is not necessarily an intuitive result, since all syngas mixtures have a very high N_2 dilution and just a fraction of H_2 .

Hydrogen content in syngas depends on the reformer used for its production. The best performing reformers were EGR³. These produced syngas with the highest H_2 content by using the exhaust gases that would normally be wasted. These reformers as their name implies, act as hybrid regenerator-reheat systems as part of the energy comes from the exhaust and part from

4.7 Acknowledgement

oxidizing methane. Also, heat goes both into the endothermic reforming reactions enhancing the chemistry of the fuel, and back into the fuel inlet. Future work should focus on obtaining the details of these processes to determine flow rates, energy spent and the overall efficiency. Nevertheless, EGR³ are a promising idea to boost reactivity while reusing the otherwise wasted energy in the exhaust gases.

In the end, this study shows that biogas-syngas-air blends are capable of achieving laminar flame speeds similar to methane-air mixtures while keeping the post-flame temperature of the combustor constant. Moreover, the syngas that boosts its reactivity is produced from the exhaust gas of the turbine, reusing energy that would otherwise be wasted. This means that biogas and other low calorific fuels can use their own exhaust to boost their reactivities and operate at typical methane conditions.

The increase of reactivity is not necessarily a positive result for a GT. Too much, and auto-ignition can happen as seen on the adiabatic reformer case. In reality, a system will not be designed to be close to an adiabatic case, but rather at an intermediate point. Also, a reforming system that uses more endothermic reactions such as steam reforming may be used to lower the output temperature and increase H_2 content in syngas. The amount of H_2 and the temperature needed from the output of the reformer to be in an optimal regime is unknown. Additional optimization is required to maximize reactivity and H_2 content without getting into the auto-ignition regime.

4.7 Acknowledgement

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5

Discharge Characterization for Methane Reforming

5.1 Preface

This chapter presents the characterization results of an atmospheric pressure nanosecond repetitively pulsed discharge for methane partial oxidation. The work was planned and executed by P. D. G. Maqueo. M. Maier performed initial spectroscopic and gas analysis measurements. M. D. G. Evans provided guidance on spectroscopic measurements and a code to create synthetic $N_2(C^3\Pi_u - B^3\Pi_g)$ emission spectra. Supervision of the research and reviewing of the manuscript, were shared between by J. M. Bergthorson and S. Coulombe. The citation for this chapter is:

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5.1 Preface

In Chapter 4, it was determined numerically that syngas produced from a reforming process can be used to enhance the reactivity of low-calorific fuels. However, the reformer was treated as a black box where chemical equilibrium is reached. In reality, high temperatures are used to achieve chemical conversion through this process within a reasonable time. Instead of heating, another methodology is using a non-thermal plasma as an energy input. In this chapter, a nanosecond repetitively pulsed discharge is used to produce a plasma inside a partial oxidation reactor. To change the applied voltage with a fixed rise-time pulse generator, the inter-electrode distance was controllable. With this setup, two regimes were observed and characterized: a diffuse and a filamentary regime. Energy per pulse was calculated from electrical measurements, temperature and electron number densities were estimated from acquired optical emission spectroscopy measurements, and conversion capabilities were determined for both regimes using a gas chromatograph.

It was found that there was a stark contrast between both regimes, except for the gas temperature in the discharge, which remained low in both cases. The low-power diffuse regime had negligible conversion efficiencies while the filamentary regime reached 26 %, producing 20 % hydrogen in the products, which could be enough to produce a change in reactivity for practical applications as seen in Chapter 4. The filamentary regime was only slightly hotter than the diffuse regime, which suggests the process is not driven by the thermal input of the discharge.

Regimes of an Atmospheric Pressure Nanosecond Repetitively Pulsed Discharge for Methane Partial Oxidation

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Abstract. The operation of a nanosecond repetitive pulsed discharge for partial oxidation of CH₄ is characterized at atmospheric pressure and room temperature. Two regimes are observed: diffuse and filamentary. The first is a low power regime, characterized by low rotational temperatures around 400 K. The second is much more energetic with rotational temperatures close to 600 K. Both have vibrational temperatures of at least 10 times their rotational temperatures. The average electron number density was determined to be 8.9×10^{15} and 4.0×10^{17} cm⁻³, respectively, showing an increase in the ionization fraction in the more powerful filamentary regime. Results of CH₄ conversion to H₂, CO, CO₂ and C₂H₆ are presented for the filamentary regime, while the diffuse regime shows no measurable conversion ability. As expected, oxidative mixtures show higher conversion ability than pure CH₄. A maximum conversion efficiency of 26.3 % and a maximum energy efficiency of 19.7 % were reached for the oxidative mixtures.

5.2 Introduction

Recently, due to an increase in energy demands and an increase in air pollution, clean and renewable energy sources have gained interest in the scientific community. Biogas, for instance, is a renewable source produced through the decomposition of organic matter. However, its low reactivity and energy content could be problematic when applied to low emission combustion technologies, such as lean premixed gas turbine engines. Fuel reformers are an interesting technology that can enable biogas and other renewable low reactivity fuels [145] for low emission combustion applications. Moreover, hydrocarbon reforming produces hydrogen and carbon monoxide, which can be used in solid-oxide fuel cells for power generation [8, 9, 10], as well as Fischer-Tropsch synthesis of higher order hydrocarbons [6, 7].

Traditionally, three main processes for hydrocarbon reforming are used: steam reforming (SR), partial oxidation (POX) and autothermal reforming. All of these are normally carried out at high temperatures and often rely on the use of transition-metal catalysts [4, 11, 12, 13]. Therefore, problems such as soot formation and catalyst deactivation often occur [4].

Plasma reforming offers an attractive alternative to these processes and has the ability to produce highly reactive species without a catalyst [16, 17]. In fact, thermal plasmas have been studied for this application [22, 19, 20], and have shown high conversion efficiencies. However, these methods are not much different from a thermal process as the gas temperature can be on the order of thousands of Kelvin, making some of these even less efficient than traditional chemical reactors [21]. Alternative to this is the use of low-temperature and low-pressure non-equilibrium plasmas, which are also very well-known [146, 147, 148] for this application. However, operating below atmospheric pressure is not industrially feasible for high throughput processes.

Other technologies, such as dielectric barrier discharges (DBDs) [23, 24, 25], gliding

5.3 Experimental Methodology

arcs [26, 27, 28], and nanosecond repetitive pulsed (NRP) discharges [29, 30, 31, 32, 33], operate at atmospheric pressure or above, and are of current interest as fuel-reforming technologies. Recently, short-duration pulsed plasmas have shown promising results [29, 30, 31, 32, 33] for CH₄ reforming. Pulses with durations of tens of nanoseconds and voltages ranging from 10 kV [36] up to 120 kV [37] are applied to produce highly reactive plasmas. The high instantaneous power input of tens of kilowatts produces high energy particles that lead to a strongly reactive plasma with a high degree of disequilibrium. Short-duration, repetitive, high-voltage pulses produce plasmas with high vibrational temperatures, which is known to be one of the main advantages of this technology. Dissociation through vibrational excitation requires a lower activation energy when compared to thermal dissociation [31, 34, 35].

In this work, NRP discharges are used to carry out partial oxidation at atmospheric pressure and room temperature. The input voltage of the discharge is varied, producing different discharge regimes. Optical emission spectroscopy is used to analyse the emission of the discharge for each regime while the reformed gas stream is analysed using gas chromatography. To probe the nature of the oxidative processes, gas composition was changed from pure CH_4 to O_2 - and air-containing mixtures.

5.3 Experimental Methodology

5.3.1 Gas discharge reactor and electrical diagnostics

Figure 5.1 shows the gas discharge assembly. The electrode configuration is a pin-to-mesh assembly. The reactor is enclosed in a quartz tube (20 mm I.D. and 22 mm O.D.) for optical accessibility. A stainless steel needle (22-gauge) embedded in non-porous alumina acts as both the gas inlet and anode of the discharge cell. The dual purpose of the needle maximizes the amount of gas treated with the discharge since the only exit point is the location where the



Figure 5.1: Schematic of the experimental setup.

plasma is formed. The ceramic holder serves as electrical and thermal insulation. A homemade NRP generator is connected to the needle. The pulse generator uses magnetic pulse compression (MPC) to achieve short pulses on the order of 100 ns with a peak voltage of over 40 kV and a maximum energy output of 14 mJ [108]. The pulse repetition frequency was set at 1 kHz, producing atmospheric pressure discharges between the needle and a grounded mesh. To reach the desired voltage amplitude, while controlling regime transitions, the ground mesh is mounted on an axial translation stage. This configuration allows the inter-electrode distance to be varied in increments of 0.15 cm. Electrical characteristics of the discharges were determined using a passive high-voltage probe (Tektronix P6015A, 75 MHz bandwidth) to measure the applied voltage and a Rogowski coil (Pearson Electronics 110 A, Model 411, 10 A/V) for the current.

5.3.2 Gas delivery and analysis

Three different gas mixtures were used as reactant feedstocks to study the different regimes of CH_4 partial oxidation: Pure CH_4 , CH_4 -air and CH_4 - O_2 . These mixtures were injected with a

total flow rate (Q) of 100 sccm using calibrated mass flow controllers (Brooks 5850s) at room temperature. The CH₄ to O₂ ratio in the CH₄-air and CH₄-O₂ mixtures is set permanently to 2:1, or an equivalence ratio (ϕ) of 4. To determine the gas temperature (detailed in Section 5.4.2), certain mixtures were seeded with 10 sccm of N₂. The pressure inside the reactor was 1 atm. The input gas mixtures and discharge products were analysed with a gas chromatograph (GC, Agilent 6890) equipped with a calibrated thermal conductivity detector (TCD).

5.3.3 Optical emission spectroscopy

The optical emission spectroscopy (OES) setup used in this work is also included in Figure 5.1. Emission from the plasma is collected using a biconvex lens (f = 300 mm) and focused onto a 200 μ m optical fibre using a biconvex lens (f = 100 mm). The resulting spot-size diameter from which light is acquired is 600 μ m and is located next to the anode as shown in Figure 5.1. Light is collected with a wavelength-calibrated spectrometer (Acton, SP2300i, 30 cm focal length) equipped with an intensity-calibrated CCD camera (Princeton Instruments PIXIS 256) with 26 μ m pixels. The wavelength resolution of the spectrometer is 0.4 nm. Integration times varied depending on emission intensity; H_{α} measurements had an integration time of 200 ms while N₂ emission was integrated for 20 ms. All parameters deduced from OES measurements are line-of-sight averaged values.

5.4 Results and discussion

Figure 5.2 shows two long-exposure digital photographs taken with an ISO sensitivity of 6400, and a lens with a focal length of 55 mm and an aperture of f/5.6. Similar to what was observed in air [36], two regimes were identified for all gas mixtures: a diffuse and a filamentary regime. The first has qualitative characteristics similar to a DC glow discharge, but it is free of observable structures, such as a cathode glow or Faraday dark space. The discharge is a

5.4 Results and discussion



Figure 5.2: Digital photograph of the: a) diffuse (1 s exposure time) and b) filamentary regime (0.005 s exposure time) in pure CH_4 plasma.

streamer, or an ionization front, that propagates from anode to cathode and bridges the two electrodes uniformly. This type of discharge has been characterized in single-pulse mode for active particle production [149]. From the digital image of Figure 5.2 (a), it is observed that the discharge occupies most of the volume of the plasma reactor. The emitted light in this regime is relatively dim but can be observed with the naked eye, having the strongest emission near the anode. By contrast, the filamentary discharge is a spark. The discharge connects the anode to the cathode with a thin high current (8 – 14 A) filament, and the light emission is of significantly higher intensity than the diffuse discharge. Figure 5.2 (b) shows the overlap of several discharge filaments observed in this regime. The discharge attachment at the cathode is located at a random position along the *r*-axis of the mesh.

Other regimes of unstable and short duration discharges were observed, marking a transition between the stable regimes. The first was a corona discharge similar to the diffuse regime but without bridging both electrodes. The discharge would either transit to the diffuse regime or extinguish and have no observable emission. The second was a mixed diffuse-filamentary discharge, which had bright filaments and a diffuse volumetric plasma at the same time. The latter could be observed between the filamentary and diffuse regimes. This regime was avoided in this work, as OES measurements were not reproducible and electrical measurements were sporadic.

The observed regimes in Figure 5.2 are only both attainable if the inter-electrode distance (d) falls within the range of 1.2 to 2.1 cm. When d is less than 1.2 cm, only the filamentary regime is observable. Conversely, when d is more than 2.1 cm, the filamentary regime cannot be produced. When d is set within a range of 1.2 to 2.1 cm, the plasma reactor can produce diffuse and filamentary regimes at different applied voltages. Seven equally spaced positions between these limits were studied in this work.

5.4.1 Electrical characteristics

The electrical characteristics of the discharge were first studied qualitatively for each mixture, identifying the breakdown voltage threshold and the boundary between the diffuse and filamentary regimes. The results are shown in Figure 5.3 which shows the discharge regime versus the peak applied voltage (V_{peak}) and the inter-electrode distance. The diffuse regime exists in a very narrow V_{peak} range for any given distance d. This is readily observable in pure CH₄ as well as in the CH₄–O₂ mixture which strongly correlate with the difficulties of avoiding a mixed diffuse-filamentary regime when attempting to sustain a discharge in the diffuse regime. In contrast, the diffuse regime in CH₄–air mixtures was remarkably stable and had a larger permissible range of V_{peak} with increasing d as seen in Figure 5.3 (centre). This larger range of V_{peak} is associated with the presence of nitrogen in the fuel-oxidizer mixture.

The presence of nitrogen in the discharge gas enhances the production of precursor electrons ahead of the streamer as computationally investigated by Naidis for CH_4 -air mixtures [61]. These electrons are the result of the photoionization of O_2 by absorption of UV photons emitted by excited N₂. There is a space-charge change due to the presence of the photoionization electrons, leading to a decrease in the electric field ahead of the streamer. However, part of the UV photons are absorbed by CH_4 , reducing the number of photoionization reactions occurring



Figure 5.3: Domain of existence of the diffuse and filamentary discharge regimes.

and leading to an increase in space-charge gradient in the streamer head. Therefore, streamers formed in the presence of N₂ have lower electric fields ahead of them, resulting in a lower streamer propagation speed [61, 150]. Additionally, a fraction of the electron energy may be consumed through the production of vibrationally excited species in N₂ containing mixtures, which also reduces the streamer propagation speed. In contrast, with no N₂, streamers have a higher propagation speed, which will more easily trigger the transition towards a spark. Hence, for a given applied voltage, pure CH₄ and CH₄–O₂ mixtures produce faster streamers, resulting in a narrower V_{peak} range for the diffuse regime.

Figure 5.4 shows characteristic voltage and power waveforms for each regime. For a given d, the applied voltage is increased up to the highest permissible value (V_{diff}) in the diffuse regime before transitioning to a filamentary discharge, as outlined by the regime transition limit in Figure 5.3. In the diffuse regime, the MPC generator produces a bipolar pulse of increasing magnitude and decreasing pulse width as the input voltage is increased. These characteristics are due to the saturation time of an internal magnetic switch of the MPC generator. By increasing the input power of the high-voltage pulse generator, the discharge transitions from one regime to the other. The transition is characterized by a streamer capable of reaching the cathode, bridging both electrodes with a conductive filament. This changes the load in the discharge



Figure 5.4: Voltage and power waveforms of CH_4 -air discharges taken at different inter-electrode distances (d1 to d7). Individual waveforms are shifted 0.5 μ s in time for clarity.

gap from mainly capacitive to resistive, triggering a collapse of V_{peak} and an increase in the discharge current and power. In the filamentary regime, the applied voltage is set to the minimum permissible value (V_{fil}) for which the discharge is stable before transitioning back to the diffuse regime. The bipolar nature of the waveform is no longer observed, as all of the circuit energy is delivered to the load (plasma), rather than shorted to the ground by the internal magnetic switch. For this case, the full-width at half-maximum (FWHM) of the voltage pulse does not depend on the voltage amplitude, as seen in Figure 5.5, but rather on the gas in the discharge gap and its ability to dissipate current.

Assuming an electrostatic field and a temperature of 600 K, it is possible to estimate the



Figure 5.5: Pulse width as a function of peak discharge voltage.

reduced electric field E/n, where E is the electric field in V/cm and n is the number density in cm⁻³. The unit of the reduced electric field is Td (Townsend), where 1 Td corresponds to 10^{-17} V·cm². Goldberg et al. [151] observed that the electrostatic assumption is valid until breakdown occurs, which is approximately at 90 % of the maximum applied voltage. Breakdown also corresponds to the maximum applied E. Using a 2D axisymmetric finite element model of the discharge cell and 90 % of V_{peak} as the boundary conditions at the needle, the maximum E/n is estimated for both regimes to be 4000 Td near the edge of the needle and 2000 Td at the centerline. The field falls to 1000 Td at 0.1 cm away from the needle in the axial direction.

As observed by Lotfalipour et al. [30], the discharge in both regimes has a first stage characterized by the charging of a capacitor with capacitance C formed by the high-voltage electrode needle, gas and ground electrode. The streamer or spark filament has not begun to propagate from anode to cathode at this point, hence the only current measured is the

displacement current (I_d) from the charging of capacitor C. This is given by:

$$I_{\rm d} = C \frac{\mathrm{d}V}{\mathrm{d}t},\tag{5.1}$$

where V is the applied voltage and t is time. The fact that the displacement current is dependent on the voltage waveform and that there is no other current present during the first stage, it is possible to measure the capacitance of the discharge gap to be from 8 to 11 pF.

Upon determining I_d , it is possible to calculate the conduction current (*I*), discharge power (*P*) and energy per pulse (U_{pulse}). Peak power increases with increasing applied voltage for both regimes reaching a maximum close to 400 kW. In the diffuse regime, there is a second peak observed, pointing to a second discharge event that can be associated to the bipolar nature of the voltage pulse. This second pulse is observed when the negative voltage pulse amplitude surpasses the breakdown limit observed in Figure 5.3.

Figure 5.6 (left) shows V_{peak} while Figure 5.6 (right) shows U_{pulse} as a function of d for all mixtures and regimes. For both discharge parameters, there is a quasi-linear increase with increasing d. The highest values of V_{peak} measured were in the diffuse regime, up to a maximum of 35.2 kV achieved by the CH₄–O₂ mixture at d = 2.1 cm. Conversely, the lowest values of V_{peak} were measured in the filamentary regime, with pure CH₄ having the minimum values, reaching a value of 25 kV at d = 2.1 cm. However, the differences in voltage peaks are small when compared to the difference in the energy deposited per pulse. The highest U_{pulse} is obtained with the CH₄–O₂ mixture, for all values of d explored in the filamentary regime, reaching a maximum of 13.9 mJ at d = 2.1 cm. In contrast, with the same mixture and d, the lowest value was observed in the diffuse regime with a value of 1.3 mJ. For d = 2.1 cm this shows that while the voltage decreases by a factor of 1.4, the energy increases 10 times from the diffuse to filamentary regime.



Figure 5.6: Peak discharge voltage and energy deposited per pulse as a function of inter-electrode distance.

5.4.2 Gas temperature

The amount of energy deposited into the gas is directly related to the overall energy efficiency of the reforming process. However, energy may be deposited into the gas in several ways. For gas heating, energy is delivered amongst rotational and translational modes while, for high chemical reactivity, it is transferred along vibrational and electronic modes. This means that, for the same amount of energy input, the process can vary in efficiency. Temperature measurements offer a way to characterize the plasma, providing insight as to how energy is being distributed in the reforming process.

In a molecular gas plasma, distributions amongst internal energy modes are given by the neutral gas temperature (translational), T_0 , rotational temperature, T_r , vibrational temperature, T_v , and electron temperature, T_e , respectively. In the particular case of non-equilibrium discharges, these temperatures are not the same, typically yielding higher T_e and T_v when compared to T_0 [71]. Characterizing these temperatures can illustrate the departure from equilibrium in the plasma. Additionally, for N₂, T_r relaxes very fast, resulting in $T_r \approx T_0$, making it a good approach to estimate the gas temperature [152]. For this reason, N₂ was injected for



Figure 5.7: Experimental and simulated emission from the 0-0 and 1-1 vibrational bands of the second positive system of $N_2(C^3\Pi_u - B^3\Pi_g)$. Experimental emission was acquired with an exposure time of 20 ms.

the non CH₄-air mixtures, as described in Section 5.3.2. To determine both T_v and T_r of the gas, the emission spectrum of the discharge in the spectral region of the second positive system of N₂($C^3\Pi_u - B^3\Pi_g$) was measured and fitted to a simulated emission spectrum. Figure 5.7 shows one characteristic example of this approach.

The emission spectrum of N_2 was simulated using a line-by-line radiation code [56]. Both T_r and T_v were calculated through non-linear optimization, minimizing the root mean square (RMS) of the error [153].

Figure 5.8 shows the calculated T_r and T_v as a function of U_{pulse} . In both discharge regimes, T_r and T_v are relatively independent of U_{pulse} . T_r remained low and closer to room temperature in the diffuse regime. T_r is close to 400 K for both oxygen-containing mixtures and near 500 K in pure CH₄. The filamentary regime showed comparable trends but with slightly higher T_r . These results indicate that even though the spark has a substantial increase in conduction current, as can be inferred from the voltage and power waveforms seen in Figure 5.4, the short pulse



Figure 5.8: Calculated $T_{\rm r}$ and $T_{\rm v}$ as a function of $U_{\rm pulse}$.

prevents a high degree of thermalization of the plasma channel, keeping it relatively cool and close to the diffuse regime. The hottest plasma observed had a T_r of 691 K at an U_{pulse} of 12.41 mJ in pure CH₄. However, the plasma channel does not have a uniform temperature, as seen in previous numerical simulations [154]. The core of the spark, for instance, has higher temperatures than the outer surface of the filament. In this work, all presented measurements are line-of-sight integrated and averaged in time. This is especially important in the filamentary regime, as the acquisition spot-size is an order of magnitude larger than the plasma channel, and multiple filaments are averaged during the acquisition time. Emission, from the outer and colder zones in the filament, will always be captured with a line-of-sight diagnostic which integrates along the whole filament volume. The latter could potentially cause an underestimation of the
spark temperature.

It has been shown that the accuracy, when determining T_v using the available vibrational bands, is low [155]. Moreover, the overall T_v might not be the same for all gaseous species in the discharge, especially in a NRP discharge, where the assumption of Boltzmann equilibrium may not hold. However, the measurements can be used as an indicator of the degree of disequilibrium and can show the thermalization trend.

In the diffuse regime, T_v is more than 10 times higher than T_r , reaching a value near 6500 K in pure CH₄, while oxygen-containing mixtures are close to 5500 K. The filamentary regime is different for each mixture. The CH₄-air plasma has a T_v close to 6000 K, while for the CH₄-O₂ plasma, it remains near 5500 K. Pure CH₄ plasma shows a slight decrease in T_v , changing from 6200 K to 5500 K, suggesting an increase in the degree of thermalization.

5.4.3 Electron number density and ionization fractions

The electron number density (n_e) is a key parameter for the characterization of discharges. This is especially important for processing plasmas used for fuel-reforming, where electron impact reactions are responsible for both the initiating and driving mechanisms. To determine n_e , line broadening is used as it is a well-established technique [156]. However, it is important to properly determine all broadening sources to extract an accurate value.

Figure 5.9 (left) shows the H_{α} line of the Balmer series observed from a diffuse and a filamentary discharge in pure CH₄. The H_{α} line has six broadening sources: instrumental $(\Delta \lambda_{instr})$, natural $(\Delta \lambda_{nat})$, resonance $(\Delta \lambda_{res})$, Doppler $(\Delta \lambda_{Doppler})$, van der Waals $(\Delta \lambda_{Waals})$ and Stark broadening $(\Delta \lambda_{Stark})$. Appendix A gives the details on the calculation of each broadening source. However, only the Stark broadening depends on n_e and, therefore, the width of the H_{α} line can be used to estimate n_e .



Figure 5.9: Characteristics of the H_{α} line in a diffuse and a filamentary regime of a CH₄ plasma: The experimental profiles observed (left) and the broadening contributions (right).

Gigosos et al. [157] calculated the Stark broadening and provided tables of $\Delta\lambda_{\text{Stark}}$ correlated with n_{e} and T_{e} for specific values of a different reduced mass μ^* . The latter is defined as $\mu^* = \mu(T_{\text{e}}/T_0)$ and accounts for the disequilibrium of the plasma. With $\mu \approx 1$ for electron-neutral interactions, μ^* only depends on the degree of disequilibrium in the plasma. Although T_{e} is not determined, T_{v} for N₂ is at least 10 times T_0 , and if $T_{\text{e}} \ge T_{\text{v}}$, then $\mu^* \ge 10$. However, the chosen data table corresponds to $\mu^* = 10$, since there is no data for a higher degree of disequilibrium. An expression was fitted to the data in the tables as shown in Appendix A, resulting in:

$$\Delta \lambda_{\text{Stark}}[\text{nm}] = \left(-1.4 \times 10^{-23} n_{\text{e}} \left[\text{cm}^{-3}\right] + 8.4 \times 10^{-7}\right) T_{\text{e}}[\text{K}] + 3.9 \times 10^{-13} n_{\text{e}} \left[\text{cm}^{-3}\right]^{0.72636}.$$
(5.2)

The error due to the uncertainty of the degree of disequilibrium is estimated by calculating the deviance of the results, using data tables correspondent to $\mu^* < 10$. Also, the term T_e appears in Equation (5.2), so an estimation is needed. Assuming the excitation temperature T_{exc} is close to T_e , it is possible to estimate its value, supposing a Boltzmann distribution [158] and using the intensity of the H_{α} and H_{β} lines. This results in $T_{\rm exc} \approx 3600$ K for the diffuse regime and $T_{\rm exc} \approx 3000$ K for the filamentary regime. These values are a very rough approximation as the H_{β} line intensity is very low and is overlapped by the C₂($A^3\Pi_g - X^3\Pi_u$) emission. Also, it is possible that for short duration pulses, the assumption of a Boltzmann distribution may not be applicable. Hence, these temperatures are taken as the lower bound for $T_{\rm e}$. The upper bound was set to 50000 K for the diffuse regime as calculated for a similar discharge in CO₂ [159], and 10000 K for the filamentary regime, which was the $T_{\rm e}$ assumption in a similar study with N₂ and N₂-H₂O plasmas [160]. Figure 5.9 (right) shows a comparison between each of the broadening sources as $n_{\rm e}$ increases, with $T_{\rm e} = 10000$ K and $T_0 = 608$ K. The Stark broadening increases with $n_{\rm e}$ and becomes the largest source after $n_{\rm e} > 5 \times 10^{16}$ cm⁻³.

Figure 5.9 (right) shows that the diffuse regime is below the point where the Stark broadening is the largest source, which makes the calculation of n_e sensitive to errors in the determination of other broadening sources. This introduces an undetermined $\Delta\lambda$ uncertainty, assumed to be 0.1 nm, which is on the same order of magnitude as the largest broadening source. Figure 5.10 shows the calculated n_e , where the error bars account for the uncertainty in μ^* , T_e and $\Delta\lambda$. These values of n_e are the result of OES measurements at the tip of the high-voltage electrode, where the electron density is usually higher than other parts of the plasma [161, 162, 163]. For the diffuse CH₄-air and CH₄-O₂ discharges, results are not shown because the H_{α} line emission is overlapped with uncharacterized emission bands. For all other experimental conditions, there is no correlation between n_e and U_{pulse} . However, n_e differs by more than an order of magnitude between regimes. The diffuse regime has an average n_e of 8.9 × 10¹⁵ cm⁻³ with an uncertainty that spans an order of magnitude, while the filamentary regime has a density of 4.0 × 10¹⁷ cm⁻³. The calculated densities result in ionization fractions of approximately 0.07 % and 3.28 %, respectively. The results presented in Figure 5.10 suggest that the amount of ionization collisions is weakly dependent on U_{pulse} , but depends strongly on the discharge regime.



Figure 5.10: Electron number density calculated from the Stark broadening of H_{α} lines.

5.4.4 Conversion characteristics

The gas chromatography measurements of the gaseous products reveal only trace amounts of H_2 produced by the diffuse regime, but with the H_2 signal lower than the sensitivity limit of the instrument. For this reason, there are no conversion results presented for these conditions. On the other hand, Figure 5.11 shows the filamentary regime conversion results, where the Specific Energy Input (SEI) is correlated with the molar fraction of H_2 , CO, CO₂ and C₂H₆. The SEI is defined as:

$$SEI = \frac{\nu U_{\text{pulse}} RT_i}{Qp},$$
(5.3)

where ν is the repetition frequency, T_i is the temperature of the reactants (300 K), p is the pressure and R is the universal gas constant. The results show an increase in conversion as SEI increases. When pure CH₄ is used, up to 2.5 % of C₂H₆ is produced, which is high when compared to the other mixtures. This suggests that methyl groups CH₃ are preferably



Figure 5.11: Resulting product molar fractions for each gas mixture in the filamentary regime as a function of SEI.

recombining to C_2H_6 instead of continuing on the dehydrogenation route. Unsaturated hydrocarbons, C_2H_2 and C_2H_4 for instance, that balance carbon species conservation between products and reactants were observed, but were not quantified. Also, both oxidative gas mixtures lead to more H_2 production. At first, it would appear that the mixture with O_2 has a better conversion performance with an H_2 output ranging from 9.4 % to 20.4 %. But, the content of N_2 in the air mixture gives an apparent reduced product output, which goes from 3.2 % to 10 % for H_2 . A clearer picture can be obtained by analysing the amount of CH_4 that has been converted, and out of this, how much is being transformed into H_2 and CO. These parameters are defined as the conversion efficiency (CE), H_2 selectivity (S_{H_2}) and CO selectivity (S_{CO}) respectively:

$$CE = \frac{n_{CH_4}^i - n_{CH_4}^o}{n_{CH_4}^i} \times 100,$$
(5.4)

$$S_{\rm H_2} = \frac{0.5n_{\rm H_2}^o}{n_{\rm CH_4}^i - n_{\rm CH_4}^o} \times 100, \tag{5.5}$$

$$S_{\rm CO} = \frac{n_{\rm CO}^o}{n_{\rm CH_4}^i - n_{\rm CH_4}^o} \times 100, \tag{5.6}$$

where n^{o} is the output number of moles and n^{i} the input number of moles. Figure 5.12 left

5.4 Results and discussion

shows CE as a function of SEI, where it is clear that the performance of both oxidative mixtures is similar, reaching up to 26.3%, and better than for pure CH₄ which has a maximum of 5.3%. Figure 5.12 right shows S_{H_2} and S_{CO} as a function of SEI, where S_{CO} is higher for the oxidative processes at 60.0%, compared to 41.5% for pure CH₄. This means that besides conversion, the introduction of oxidative species increases H₂ production. However, a S_{CO} of 80.0% is relatively high and means that reforming also favours oxidative processes leading to CO and CO₂. The selectivities appear constant with respect to the energy input, which points to a dependence on the stoichiometry of the mixture and not on the discharge characteristics.



Figure 5.12: Conversion efficiency and selectivity of H_2 and CO for each gas mixture in the filamentary regime as a function of SEI.

The energy efficiency of the discharge for partial oxidation was evaluated using the low heating value (LHV) and mass (m) of the fuels in both the products and reactants, as seen in the following expression:

$$\eta = \frac{\sum (\text{LHV}_{\text{prod}} \cdot m_{\text{prod}})}{U_{\text{pulse}} + \text{LHV}_{\text{CH}_4} \cdot m_{\text{CH}_4}} \times 100.$$
(5.7)

The expression evaluates the ratio of converted energy to a given energy input by both the discharge and the reacting gas. Figure 5.13 shows a linear increase in energy efficiency with

increasing SEI. The energy efficiency follows similar trends to the conversion efficiency, resulting in both oxidative mixtures having an energy efficiency of up to 19.7 % while pure CH_4 reached a maximum of 4.8 %. This is a result of the difference in energy requirements of the exothermic oxidative process and endothermic CH_4 dehydrogenation through electron impact.



Figure 5.13: Energy efficiency of the discharge for each gas mixture in the filamentary regime as a function of SEI.

The efficiency of this reactor is similar to a DBD as seen in the work by Nozaki et al. [102]. However, there are two parameters that can be altered to improve the efficiency of the process. The first is the minimization of dead volume of the reactor. With a 20 mm I.D. and assuming the plasma filament diameter is in the 100 micron range, only 0.0025 % of the volume of the reactor is in contact with the plasma. Moreover, with a pulse width of 100 ns and a period of 1 ms between pulses, the duty cycle is 1/10000. This leaves all the gas that has left the vicinity of the filament untreated. One simple way to decrease the dead volume is to reduce the size of the reactor. Another possibility is to increase the pulse repetition frequency. This would also

5.5 Conclusions

imply an increase in SEI as seen in Equation 5.3. Figure 5.13 shows that an increase in SEI suggests an increase in efficiency. However, it is unknown how much the efficiency is going to be scaled by the increase in pulse repetition frequency. The latter is something that remains to be explored. The second parameter is the use of a catalyst that would lower the activation energy of CH_4 dehydrogenation reactions and could have a synergistic effect with the plasma [18, 55, 164]. A catalyst which lowers the activation energy of the process could enable the use of the diffuse regime, which would also increase the amount of gas treated by the discharge.

5.5 Conclusions

Using a pin-to-mesh plasma source, different regimes of a nanosecond pulsed discharge were studied at atmospheric pressure and room temperature and used for CH_4 partial oxidation. Two stable operation regimes were identified: diffuse and filamentary. Electrical diagnostics, optical emission spectroscopy and gas chromatography were used to characterize the performance and applicability of each discharge regime for CH_4 conversion to syngas.

Qualitative analysis of the discharge revealed the threshold voltages for breakdown and regime transition. This showed that the diffuse regime exists over a narrow range of applied peak voltages, for a given pin-to-mesh distance. The operability range is dependent on the gas composition, with N_2 -containing mixtures having the largest range. The analysis also showed that the pulse width was dependent on the applied voltage in the diffuse regime while it remained constant in the filamentary regime. This suggests that the pulse width was controlled by the pulse generator circuit in the diffuse regime and by the gas chemistry in the filamentary regime.

Further electrical analysis showed that, the peak applied voltage is reduced by a factor of 1.4 from the diffuse to the filamentary regime, while the deposited energy increased more than 10 times. The difference in deposited energy is one of the most notable changes with regime

transition.

Optical emission spectroscopy was used to estimate the temperature of the gas and electron number density. Temperature analysis revealed a slight difference in gas temperature between both regimes, the filamentary regime being slightly hotter than the diffuse regime. It was also shown that both discharge regimes lead to a high degree of disequilibrium, having vibrational temperatures close to 10 times higher than their rotational temperatures. This results in a warm plasma, where the gas is heated by the discharge but the rotational and vibrational temperatures are not in equilibrium.

The electron number density analysis showed a marked difference between both regimes. The filamentary regime shows an electron number density of more than an order of magnitude higher than the diffuse regime. Also, it was shown that the electron number density has no correlation with deposited energy per pulse, which means that the electron number density is only regime dependent.

The diffuse regime was unable to produce detectable amounts of any converted product. We hypothesize that there are only few collisions that have more energy than the activation energy. Conversely, the filamentary regime produced a measurable amount of converted products. Higher temperatures in the filamentary regime are likely the reason why this happens. The conversion results showed an almost linear increase in both conversion efficiency and energy efficiency with respect to specific energy input. Finally, oxidative mixtures proved more efficient in both cases. Selectivity in contrast, appeared constant with respect to energy input.

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Appendix A. Broadening sources

There are six broadening sources for the H_{α} line of the Balmer series. Each broadening source produces a specific profile and is measured at FWHM. The instrumental and Doppler mechanisms produce an approximately Gaussian profile, and the rest, an approximately Lorentzian profile. The convolution of these profiles results in a Voigt profile. Hence, the total broadening of the H_{α} line is not a straightforward addition of all the broadening sources. Fortunately, Olivero and Longbothum developed a high precision technique involving [165]:

$$\Delta\lambda_{\rm Lorentz} = \Delta\lambda_{\rm nat} + \Delta\lambda_{\rm Waals} + \Delta\lambda_{\rm res} + \Delta\lambda_{\rm Stark}, \tag{5.8}$$

$$\Delta\lambda_{\rm Gauss} = \sqrt{\Delta\lambda_{\rm Doppler}^2 + \Delta\lambda_{\rm instr}^2},\tag{5.9}$$

$$\Delta\lambda_{\text{Voigt}} = 0.5346\Delta\lambda_{\text{Lorentz}} + \sqrt{0.2166\Delta\lambda_{\text{Lorentz}}^2 + \Delta\lambda_{\text{Gauss}}^2},$$
(5.10)

where $\Delta \lambda_{\text{Voigt}}$, $\Delta \lambda_{\text{Lorentz}}$ and $\Delta \lambda_{\text{Gauss}}$ are the broadening of the Voigt, Lorentzian and Gaussian profiles.

Two contributions to the broadening of H_{α} are invariant to the plasma conditions. The first, $\Delta \lambda_{\text{instr}}$, was determined experimentally to be 0.4 nm by measuring the emission of a laser (635 nm). The other, $\Delta \lambda_{\text{nat}}$, depends on the probability of transition between the upper (*u*) or lower states (*l*) of the radiative transition and any allowed level *u'* or *l'* [166]:

$$\Delta \lambda_{\rm nat}[\rm nm] = 1 \times 10^{-9} \lambda_{ul}^2 \frac{\sum_{u'} A_{u'u} + \sum_{l'} A_{l'l}}{2\pi c}, \qquad (5.11)$$

where c is the speed of light in $m \cdot s^{-1}$ and $A_{x'x}$ is the transition probabilities between state x and

x'. For H_{α} , $\Delta \lambda_{nat} = 1.1 \times 10^{-4}$ nm.

Resonance broadening is a result of collisions between similar particles. For H_{α} , it is the interaction between two hydrogen atoms. A formula is given by Griem [156]:

$$\Delta\lambda_{\rm res}[\rm nm] = \frac{3e^2\lambda_{ul}^2}{8\pi^2\epsilon_0 m_{\rm e}c^2} \left[\lambda_{lg}f_{gl}\sqrt{\frac{g_g}{g_l}}n_g + \lambda_{ug}f_{gu}\sqrt{\frac{g_g}{g_u}}n_g + \lambda_{ul}f_{lu}\sqrt{\frac{g_l}{g_u}}n_l\right],\tag{5.12}$$

where e is the electron charge in C, m_e the electron mass in kg, ϵ_0 the permittivity of free space in F·m⁻¹, λ_{yx} is the wavelength in m of the photon emitted for a transition from electronic state y to x, f_{xy} is the absorption oscillator strength and g_x is the statistical weight of electronic state x. Considering that for H_{\alpha} the indices correspond to g = 1, l = 2 and u = 3, the constants can be found at NIST [167]: $f_{gl} = 0.41641$, $\lambda_{lg} = 121.567$ nm, $f_{lu} = 0.64108$, $\lambda_{ul} = 656.279$ nm, $f_{gu} = 0.07914$, $\lambda_{ug} = 102.5728$ nm, $g_g = 2$, $g_l = 8$ and $g_u = 18$.

The excited state number densities are a fraction of the total gas number density $(n = p(k \cdot T_0)^{-1})$. Using T_{rot} as an approximation of T_0 , the partition functions can be calculated to determine the fraction of atoms in each of the excited levels. This results in $n_g \approx p(k \cdot T_0)^{-1}$ and $n_l \approx 1 \times 10^{-51} p(k \cdot T_0)^{-1}$. The expression is reduced to depend only on the atomic hydrogen molar fraction (X_{H}) , the gas pressure (p) and T_0 in Kelvin. With 1 atm of pressure and assuming 0.25 % of atomic hydrogen as calculated by Naidis [61] for a CH₄-air discharge at 600 K (close to the measured T_{rot}), it results in:

$$\Delta \lambda_{\rm res}[\rm nm] = \frac{0.3[\rm nm \cdot K]}{T_0[\rm K]}.$$
(5.13)

Doppler broadening occurs when an emitting particle moves towards or away from the observer. The emitted photon will appear shifted in wavelength due to the Doppler effect. An

expression is given by Konjević [166] and Griem [156] for this broadening source:

$$\Delta \lambda_{\text{Doppler}}[\text{nm}] = \lambda_{ul} \sqrt{\frac{8kT_0 ln(2)}{m_{\text{H}}c^2}},$$
(5.14)

where $m_{\rm H}$ is the mass of the hydrogen atom in kg. Reducing the expression to depend only on T_0 results in:

$$\Delta \lambda_{\text{Doppler}}[\text{nm}] = 4.7 \times 10^{-4} [\text{nm} \cdot \text{K}^{-0.5}] \sqrt{T_0[\text{K}]}.$$
(5.15)

The van der Waals broadening is more complicated as it depends on the interactions between the emitter and the surrounding gas. Kelleher [168] gives the following expression:

$$\Delta \lambda_{\text{Waals}}[\text{nm}] = 8.18 \times 10^{-5} \lambda_{ul} \left(\bar{\alpha}\bar{R}^2\right)^{2/5} \left(\frac{T_0}{\mu}\right)^{3/10} n_{\text{p}},$$
(5.16)

where μ is the perturber-emitter reduced mass in a.m.u., $\bar{\alpha}$ is the average polarizability of the perturber in cm³, n_p is the perturber number density in cm⁻³ and \bar{R}^2 is defined as [169]:

$$\bar{R}^{2} = \frac{1}{2} \frac{U_{\rm H}}{U_{\infty} - U_{\alpha}} \left[5 \frac{z^{2} U_{\rm H}}{U_{\infty} - U_{\alpha}} + 1 - 3l_{\alpha} \left(l_{\alpha} + 1 \right) \right], \tag{5.17}$$

where $U_{\rm H}$ and U_{∞} are the ionization energies of hydrogen and the emitter atom respectively, U_{α} is the energy of the upper state, l_{α} is the orbital quantum number of the upper state and zis the number of effective charges. For H_{α} , as a neutral emitter, z = 1, $U_{\rm H} = U_{\infty} = 13.6 \,\text{eV}$, $U_{\alpha} = 12.09$ and $l_{\alpha} = 0$, 1 and 2 for the upper states 3s, 3p and 3d. \bar{R}^2 results in 207.3, 180.3 and 126.2 for $l_{\alpha} = 0$, 1 and 2. Using 1.6 %, 17 % and 81.4 %, which are the fraction of the total emission, as weighting factors we get $\bar{R}^2 = 136.7$.

The perturbers assumed for the mixtures used are: N₂, O₂ and CH₄, with polarizabilities of 1.8×10^{-24} cm³ [170], 1.6×10^{-24} cm³ and 2.6×10^{-24} cm³ [171] respectively. Using the molar

fraction of each component as weighting factors, $\bar{\alpha}$ is 2.6×10^{-24} cm³ for pure CH₄, 2.0×10^{-24} cm³ for CH₄-air, and 2.3×10^{-24} cm³ for CH₄-O₂.

Interactions of the hydrogen atom with larger molecules results in a $\mu \approx 1$ and with a p = 1 atm, the van der Waals broadening expression is reduced to:

$$\Delta \lambda_{\text{Waals}}[\text{nm}] = \frac{\text{A}[\text{nm} \cdot \text{K}^{0.7}]}{(T_0[\text{K}])^{0.7}},$$
(5.18)

where A is a constant that depends on the input gas mixture. A is $6.8 \text{ nm} \cdot \text{K}^{0.7}$, $6.4 \text{ nm} \cdot \text{K}^{0.7}$, and $6.1 \text{ nm} \cdot \text{K}^{0.7}$ for CH₄, CH₄-air, and CH₄-O₂ respectively.

For Stark broadening, Gigosos et al. [157] have provided tables correlating n_e in terms of λ_{Stark} and T_e . However, for the purpose of this work, λ_{Stark} was extracted and plotted in terms of n_e and T_e . With these data, an expression was fitted in two steps. First, a linear fit was done in terms of T_e for each value of n_e , resulting in an equation of the form:

$$\Delta \lambda_{\text{Stark}}[\text{nm}] = F(n_{\text{e}})T_{\text{e}} + G(n_{\text{e}}).$$
(5.19)

The second step was to fit the functions $F(n_e)$ and $G(n_e)$ to n_e . $F(n_e)$ was linearly fitted, while $G(n_e)$ was a logarithmic fit. The resulting expression is shown in Equation 5.2. The methodology for all fitting procedures was the minimization of the RMS of the error. Figure 5.14 shows a comparison of the extracted data from Gigosos et al. [157] and the fitted expression.



Figure 5.14: Fitted expression compared to data from Gigosos et al. [157].

6

Study of the Energy Efficiency in Plasma Methane Reforming

6.1 Preface

This chapter presents the study of varying reactant temperature, energy per pulse, and repetition frequency on the reforming performance and efficiency of a nanosecond repetitively pulsed discharge for methane reforming. The work was planned and executed by P. D. G. Maqueo. Supervision of the research and reviewing of the manuscript, were shared between by J. M. Bergthorson and S. Coulombe. The citation for this chapter is:

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6.1 Preface

Building off of the conclusions of Chapter 5, a new plasma source was assembled that reduced the amount of dead volume around the discharge. Additionally, a novel solid-state pulse generator was developed, capable of reaching repetition frequencies of 10 kHz with pulses that have a duration of 40 ns. This chapter presents electrical diagnostics, optical diagnostics using optical emission spectroscopy, gas temperature estimation, and composition measurements of a reformer driven by a nanosecond repetitively pulsed discharge. Methane pyrolysis, partial oxidation, and dry reforming were studied by varying the initial mixture temperature, energy per pulse, and pulse repetition frequency. The variation in each parameter produced a change in the reforming characteristics and efficiency. The effect on the reforming efficiency is quantified and compared for each of these parameter variations.

It was found that as temperature and repetition frequency increase, the applied discharge voltage reduces along with the energy per pulse. Moreover, increasing the pulse repetition frequency has a heating effect with temperatures similar to the one provided by previously heating the reactants with a flame. Optical diagnostics revealed that the relative emission intensity of the C_2 Swan bands with respect to the emission intensity of CH scale with the increase in discharge power. These results appear to be correlated with the performance of the discharge as a reformer, having higher conversion efficiencies for higher C_2 emission. In terms of reforming performance, it was found that increasing the inlet gas temperature up to 700 K had no effect on the reforming efficiency, even surpassing that of increasing energy per pulse. Reforming appears to be improved by having a certain amount of energy delivered more often, rather than having the same energy delivered in more powerful pulses that occur less often. These results can guide developments of advanced plasma-assisted reforming and technologies.

Energy Efficiency of a Nanosecond Repetitively Pulsed Discharge for Methane Reforming

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Abstract. The performance of a nanosecond repetitively pulsed discharge for CH₄ reforming is studied at atmospheric pressure for temperatures ranging from 300 to 700 K. The high-voltage pulser used is capable of producing a voltage pulse with an amplitude of 14 kV and a duration of 40 ns at a repetition frequency of 10 kHz. The discharge energy per pulse is varied in a range from 462 μ J to 2.47 mJ. The rotational temperature is estimated by fitting synthetic to experimental spectra. Experiments at pulsing frequency of 1 kHz led to temperature profiles that remain unchanged along the axial direction of the reactor. For pulse frequencies between 2 to 10 kHz, the average temperature of the filament rises from 507 to 777 K. Emission from $C_2(A^3\Pi - X^3\Pi)$ is compared to emission from $CH(A^2\Delta - X^2\Pi)$ along the reactor axis and with respect to the energy input. It is found that as the energy input increases, so does the emission from $C_2(A^3\Pi - X^3\Pi)$, turning the discharges green rather than blue. Results from CH_4 conversion show that the inlet gas temperature has negligible effect on reforming performance. Higher values of energy per pulse improve conversion and energy efficiency. However, increasing the pulse frequency leads to the best performance enhancement with a maximum slope of 0.53 % and 0.24 % per kJ·mol⁻¹ for conversion and energy efficiency, respectively. The maximum conversion and energy efficiencies were 68.2 % and 25.6 %, respectively, measured in a CH₄-air mixture.

6.2 Introduction

Our society largely depends on the combustion of hydrocarbons to meet our energy needs. However, a well-known drawback is the emission of pollutants from this process. Increasing energy demands and more stringent regulations in pollutant emissions have prompted a need for new combustion technologies and alternative energy sources. Hydrogen, for instance, burns with zero carbon footprint, produces clean electricity in fuel cells [8, 9, 10] and is applicable as a reactivity enhancer to allow cleaner operation regimes in gas turbine engines [145]. Industrially, it is mainly produced together with carbon monoxide in a well-developed process known as methane reforming [4]. Ongoing research in this field is focused on improving the efficiency of the process.

Current reforming technologies are steam reforming (SR), partial oxidation (POX), dry reforming (DR), and a combination of two or more known as autothermal reforming (AR). Methane is a stable hydrocarbon which requires a high energy input to achieve its conversion into hydrogen and carbon monoxide. These processes are typically carried out at high temperatures using transition metal catalysts [4, 11, 12, 13]. However, this poses a series of challenges ranging from the use of expensive and specialized equipment that can handle high temperatures, to catalyst deactivation from carbon contamination or sintering [4]. In this regard, plasmas are an attractive alternative technology, offering the possibility of an energy input that does not heat the bulk of the gas and provides highly reactive species [16, 17].

The use of plasma technologies for fuel reforming is not a new topic. For instance, there are applications of thermal plasma torches [22, 19, 20], dielectric barrier discharges (DBDs) [23, 24, 25], gliding arc discharges [26, 27, 28] and nanosecond repetitively pulsed (NRP) discharges [29, 30, 31, 32, 33] to fuel reforming. The latter has recently gained interest as it shows promising reforming results. Pulses with amplitude up to 120 kV [37] and duration of a

few tens of nanoseconds are applied to produce either diffuse atmospheric glow discharges or powerful sparks [36]. The high energy density delivered in short pulses creates a highly reactive gas with a high degree of disequilibrium and high vibrational temperatures. This leads to higher efficiencies, since the energy is not used to heat the gas, but rather to drive the reforming reactions. For instance, energy requirements for CO_2 dissociation are lower through vibrational excitation than thermal dissociation [31, 34, 35], which leads to an increased efficiency in dry reforming. Additionally, high vibrational temperatures are also beneficial when a catalyst is present as observed in DBD studies [102, 55, 18].

In this work, NRP filamentary discharges are used for CH_4 dehydrogenation, partial oxidation and dry reforming. Three parameters are varied to determine the most efficient energy input for fuel reforming: energy per pulse, initial gas temperature and pulsing repetition frequency. Optical emission spectroscopy is used to estimate the temperature of the plasma and characterize radical emission as a function of the previously mentioned parameters. The reformed gas is analyzed using gas chromatography to determine the composition of the products.

6.3 Experimental Methodology

6.3.1 Reactor design

Figure 6.1 shows a schematic of the reactor assembly. Electrodes are in a pin-to-plane configuration, where the pin connected to a high-voltage generator acts as the anode, and the plane connected to the ground is the cathode. The inter-electrode distance (d) is fixed at 5 mm. The pin is a 22-gauge stainless steel needle and acts as the gas inlet as well, ensuring that all reactants pass through the location where the plasma is formed, maximizing the amount of gas treated. The ground is made of brass, which is an alloy made out of copper and zinc.

Both elements have emission lines in the visible range, and are a good indicator of electrode ablation. Gases exit through a 0.7 mm hole centered in the ground plate. The electrode assembly is enclosed in a quartz tube with an outside diameter (OD) of 6.35 mm and an inside diameter (ID) of 4 mm. The quartz tube provides means for plasma confinement, electrical insulation and optical access. The anode assembly is not thermally insulated and is capable of withstanding temperatures up to 1000 K.



Figure 6.1: Schematic of the experimental setup.

Heating of the inlet gas stream is provided by a premixed methane-air flame. Electrical heating proved to be unfeasible since commercial heaters for such a small volume are not well insulated for high-voltage applications. Other electrical insulators that could withstand high voltages did not have good thermal conductivity. A flame on the other hand, does not need any electrical components and can reach temperatures in excess of 1000 K. The flame heats the anode assembly directly as seen in the schematic of Figure 6.1. Temperature is controlled by means of the fuel flow rate to the heating element, which controls the flame equivalence

ratio and total flow. To ensure steady state is reached, the flame heats the anode for one hour before experiments take place. The resulting inlet gas temperature (T_i) is measured with a thermocouple located at the exit of the needle while the plasma is off. At steady state, T_i is quite constant, with a maximum variation of 5 K.

Three different reactions are studied with this setup: pure CH₄, CH₄-air and CH₄-CO₂ mixtures. Pure CH₄ serves as a comparison mixture to separate the effects of oxidation from electron impact dehydrogenation. CH₄-air is used to compare the performance with previous work [172] and current partial oxidation efforts. This mixture has a CH₄ to O₂ ratio of 2:1 which corresponds to an equivalence ratio (ϕ) of 4. For dry reforming, a CH₄-CO₂ mixture with a 2:3 ratio is used. All gas mixtures are injected at a total flow rate (Q) of 100 sccm using calibrated mass flow controllers (Brooks 5850s). Additionally, N₂ was added as a tracer gas for OES experiments, at a rate of 3 sccm. All experiments are carried out at atmospheric pressure. Exhaust gas is collected and analysed using a gas chromatograph (Agilent 6890N) equipped with a thermal conductivity detector (TCD).

6.3.2 Nanosecond pulse generator and electrical diagnostics

The high-voltage pulser used in this study is the latest generation of our homemade diode opening switch generator. The architecture of the switching circuit is similar to others reported in the literature [29, 108]. Changes made to previous architectures increase the pulse amplitude and reduce the pulse duration at higher repetition frequencies. These result in a pulse with a maximum voltage amplitude (V_{peak}) of 14 kV and a duration of 40 ns at a maximum repetition frequency of 10 kHz. Power is delivered to the pulser using two DC power supplies in series (Sorensen, DCR 600-4.5B and Hewlett Packard, 6448B) capable of reaching up to 1.2 kV DC. Pulsing frequency is varied using a transistor-transistor logic (TTL) signal (V_{trig}) produced by a trigger pulse generator (BNC-575). Figure 6.2 shows a digital photograph of CH₄-air

(inlet gas temperature of 300 K) filamentary discharges produced by the high-voltage pulse generator between the needle and ground plane. To characterize the output of the generator, the applied voltage and current waveforms are measured with a passive high-voltage probe (Tektronix P6015A, 75 MHz bandwidth) and a wideband current monitor (Pearson Electronics Model 6585), respectively as shown in Figure 6.1. The current probe is connected to a 50 Ω terminator feedthrough (Picotech 1 W 1 GHz) to match the 1 M Ω impedance input in the digital phosphor oscilloscope (Tektronix TDS3054B, 500 MHz bandwidth, 5 GS/s).



Figure 6.2: Digital photograph with a 50 ms exposure time of CH_4 -air discharges with an inlet gas temperature of 300 K.

6.3.3 Optical diagnostics

Figure 6.1 shows the optical emission spectroscopy (OES) assembly attached to the experimental setup. All lenses and optical mounts are placed on an axial stage with a maximum travel distance of 20 mm parallel to the x axis of the reactor. Light from the plasma travels first through a fused-silica plano-convex lens (f = 100 mm). Then, it is reflected by a UV-enhanced aluminum mirror into another plano-convex lens (f = 300 mm). The latter focuses the light

passing by a high-pass filter ($\lambda > 280$ nm) and onto an optical fibre (200 µm bundle). The high-pass filter eliminates the second-order reflections from higher energy emissions. This set of lenses results in a 3:1 magnification factor and a spot-size diameter of 66 µm from which all light is collected. A wavelength-calibrated spectrometer (Acton, SP2300i, f = 30 cm) equipped with a an intensity-calibrated CCD camera with 1024 x 256 26 µm pixels (Princeton Instruments, PIXIS 256), detects the light from optical setup. The maximum resolution of the spectrometer is 0.4 nm. All OES measurements are line-of-sight averaged. Integration time varies between 1 ms and 1 s, depending on the plasma emission intensity. The experimental function of the spectrometer, used to convolve the theoretically calculated emission lines, is obtained by acquiring the emission of a He-Ne laser ($\lambda = 636.2$ nm, linewidth = 1 pm).

6.3.4 Experimental procedure

Previous work on methane partial oxidation showed that both the conversion efficiency and energy efficiency of a nanosecond pulsed discharge increase as the energy per mole or specific energy input (SEI) increases [172]. However, it is not clear if the contribution is mainly due to local gas heating, as conversion only appeared in the hotter filamentary regime. This study attempts to answer this question by varying inlet gas temperature (T_i), energy per pulse (U_{pulse}) and pulsing frequency (ν). The objective is to determine what form of energy input is most efficient for methane reforming with nanosecond pulsed discharges in the filamentary regime. Consequently, three main sets of experiments are done for three different reactant mixtures: increasing U_{pulse} at constant T_i and ν , increasing T_i at constant ν , and, finally, increasing ν at constant T_i .

6.4 **Results and discussion**

The plasma source is capable of operating in the diffuse and filamentary regime as reported in previous studies with similar conditions [172, 36, 56, 108]. Qualitatively, for high values of T_i , the discharge operates in a hybrid regime with a well defined filament in the center of the plasma and a volume of diffuse glow. Figure 6.2 shows one case of this regime. This behavior can be explained by the reduction in density as temperature increases, which favors the diffuse regime. On the contrary, higher ν causes a less-stable diffuse regime and the discharge typically turns into a bright spark. Evans et al. [56] reported that there is a limit in the amount of discharge events per volume of gas treated before the discharge transits to a spark. As ν increases, more discharge events happen for the same gas volume when the flow rate is kept constant, thus explaining this behavior.

6.4.1 Electrical characteristics

Figure 6.3 (left) shows a typical voltage waveform along with a digital photograph of the discharge. The total pulse duration is around 40 ns with a rise time of 20 ns. Duration is constant regardless of V_{peak} and ν . During the voltage rise period, before the streamer has taken off, there is no conduction current (I_c). This phase is characterized as a charging capacitor, and consequently the measured current (I_m) during this time depends only on the capacitance (C) and the voltage differential. This is known as the displacement current (I_d), and is mathematically expressed by:

$$I_{\rm d} = C \frac{\mathrm{d}V}{\mathrm{d}t},\tag{6.1}$$

The capacitor charging phase is seen in Figure 6.3 (right) as a small current peak between 20 and 40 ns, which coincides with the voltage rise time. With dV/dt obtained from the voltage waveform, C is calculated to be 0.3 pF. The displacement current, I_d , can then be calculated

throughout the pulse from Equation 6.1 and the measured V(T). The conduction current, I_c , is the result of $I_m - I_d$. Figure 6.3 (right) shows a comparison between I_m and I_c . The current pulse is of less than 20 ns in duration with a FWHM of 13 ns. Oscillations in current are considerably larger compared to the main pulse than what is observed in the voltage waveform. However, as input power is increased, current oscillations do not scale up with the main current pulse, suggesting noise as the origin. Instantaneous power is calculated by multiplying V(t) and $I_c(t)$, and results in a waveform with an amplitude of tens of kW and a duration similar to the primary current pulse. The integration of the power waveform gives the energy per pulse (U_{pulse}).



Figure 6.3: The voltage waveform with a digital photograph showing the formed CH_4 plasma at 1 kHz and 300 K (left), and the measured and calculated current waveforms(right).

The maximum U_{pulse} achieved is 2.47 mJ and is limited by the DC voltage input. This occurs with pure CH₄, $T_i = 300$ K and $\nu = 1$ kHz, which are the hardest conditions to ignite. For experiments that have increasing T_i and ν , V_{peak} and U_{pulse} are measured at the minimum stable operating conditions. Figure 6.4 shows the change in V_{peak} and U_{pulse} with respect to T_i and ν . Both lead to lower V_{peak} as T_i and ν increase. Lower V_{peak} means that the plasma becomes progressively easier to ignite, suggesting that the ionization characteristics of the gas have changed. This becomes clear with higher values of T_i where the gas is hotter and less dense.

6.4 Results and discussion

Higher values of ν are hypothesized to lead to similar characteristics, producing a temperature rise as the gas has less time between pulses to dissipate energy.

The decrease in V_{peak} is followed by a decrease of U_{pulse} for both cases. For increasing T_{i} , U_{pulse} ranges from 866 to 471 μ J. Similarly, for increasing ν , the measured values of U_{pulse} range from 922 to 462 μ J. In this regard, the change in U_{pulse} is practically the same for both parameter sweeps.



Figure 6.4: V_{peak} and U_{pulse} as temperature (left) or frequency increases (right).

6.4.2 Emission characteristics and gas temperature

This study relies on temperature measurements to compare the contributions from pre-heating reactants to the thermal and non-thermal contributions from the discharge. The inlet gas temperature, T_i , is measured with a thermocouple, while the temperature in the plasma requires non-intrusive diagnostics. It is well-known that the rotational temperature (T_r) of N₂ relaxes rapidly to the gas translational temperature (T_{gas}) [152] and consequently can be used as a reliable diagnostic of the amount of heating produced by the discharge. For this reason, N₂ is injected as a tracer gas in both the CH₄ and CH₄-CO₂ experiments, and the emission from the

second positive system of $N_2(C^3\Pi_u - B^3\Pi_g)$ is measured. Experimental spectra are compared to modeled $N_2(C^3\Pi_u - B^3\Pi_g)$ emission spectra using an in-house code and benchmarked with the commercial software SPECAIR [56]. The modeled spectra are dependent on the vibrational temperature (T_v) and T_r of N_2 . Hence, both parameters are estimated through non-linear optimization, minimizing the root mean square of the error between simulated and experimental spectra, similar to the methodology followed in previous work [172, 56, 153]. Figure 6.5 shows an example of this approach, comparing the experimental spectra obtained from pure CH₄ plasma at $T_i = 300$ K and $\nu = 1$ kHz and the modeled spectra of N_2 at $T_r = 374$ K and $T_v = 4034$ K.



Figure 6.5: Experimental and simulated emission from $\Delta v = 0$, 1 and 2 bands of N₂(C³ Π_u -B³ Π_g).

Figure 6.6 shows the estimated T_{gas} , assuming $T_{\text{gas}} \approx T_{\text{r}}$, for the three different experimental sweeps. All spectroscopic measurements were taken along the axis of the reactor in increments of 200 μ m up to 1 mm away from the electrodes, after which measurements were taken 1 mm apart of each other. Each column is one gas mixture, starting with pure CH₄ and ending with CH₄-CO₂. At $T_{\text{i}} = 300$ K and $\nu = 1$ kHz, T_{gas} barely changes for higher values of U_{pulse} .



Figure 6.6: Estimated T_{gas} along the axis of the reactor where the anode and cathode are at x = 0 and x = 5 mm, respectively. The experiments in a), b) and c) are set to $T_i = 300$ K and $\nu = 1$ kHz; d), e) and f) are set to $T_i = 300$ K and variable ν ; g), h) and i) are set to $\nu = 1$ kHz and variable T_i . The left column are experiments with pure CH₄, the center column with CH₄-air mixtures, and the right column with CH₄-CO₂ mixtures.

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The gas temperature near the electrodes goes from 410 to 480 K, and is a similar result to what was observed in a previous study of the filamentary regime [172]. In cases with increasing U_{pulse} and T_{i} , T_{gas} is relatively constant along the filament and down to ~50 K colder than the near-electrode temperature. Conversely, for increasing ν , the temperature profile has a hot middle part with lower gas temperature closer to the electrodes, only to have temperature rise again near the cathode. The temperature difference between the hot and cold zones is above 100 K, reaching a maximum ΔT_{gas} of 352 K and a near-cathode temperature of 1039 K. Overall, the temperature of the gas increases with higher values of ν . From $\nu = 2$ to 10 kHz the average temperature rise increases from 507 to 777 K.

All cases seem to have higher near-cathode temperatures. This result is accompanied by evidence of electrode ablation: emission from the plasma shows strong zinc lines at 472 nm and 481 nm, and copper lines at 510, 515 and 522 nm. This suggests that the cathode is hotter and possibly has the most favorable conditions for dissociation and reforming. It also results in contrast with temperature measurements made in an atmospheric pressure diffuse discharge, where rotational temperatures were higher near the anode [56].

When observing the plasma, it is clear that there is a variation in the visual appearance of the discharge with respect to the energy input. Color variations are due to changes in the emission intensity of the blue CH($A^2\Delta - X^2\Pi$) lines and the green C₂($A^3\Pi - X^3\Pi$) lines. For experiments with a pulsing frequency $\nu = 1$ kHz, the plasma is visually green only near the electrodes. Conversely, discharges sustained with pulsing frequencies greater than 1 kHz are visually green along the whole filament. These observations are represented in Figure 6.7, which shows the relative intensity between the strongest peak of the C₂($A^3\Pi - X^3\Pi$) band with respect to the strongest peak of the CH($A^2\Delta - X^2\Pi$) band as a function of the distance to the anode for $\nu = 1$ kHz discharges. Experiments with pulsing frequencies greater than 1 kHz are not shown for clarity in Figure 6.7 as their profiles are practically constant. The results indicate that the CH($A^2\Delta - X^2\Pi$) emission dominates the discharge channel for a pulsing frequency $\nu = 1 \text{ kHz}$, getting close to a 1:1 emission ratio near the electrodes. For pure CH₄ and CH₄-air mixtures, the average emission intensity ratio of C₂($A^3\Pi - X^3\Pi$) over CH($A^2\Delta - X^2\Pi$) is 30 %. For CH₄-CO₂ mixtures, this value is lower, at 20 %. This is also observed for emission at the electrodes, with CH₄ and CH₄-air plasmas having a peak ratio of C₂($A^3\Pi - X^3\Pi$) over CH($A^2\Delta - X^2\Pi$) of up to 87 % while CH₄-CO₂ plasmas has a maximum of 48 %. Stronger emission intensity of C₂($A^3\Pi - X^3\Pi$) is associated with a more energetic discharge [173]. Higher energy increases the degree of CH₄ dehydrogenation and thus, the production of C₂. Hence, this suggests higher reforming activity near the electrodes for $\nu = 1 \text{ kHz}$ discharges.



Figure 6.7: Relative intensity between the strongest peaks of the $C_2(A^3\Pi - X^3\Pi)$ and $CH(A^2\Delta - X^2\Pi)$ bands along the axial direction of the reactor.

This behavior can be further quantified by plotting the emission intensity ratio versus the specific energy input of the discharge. This parameter is the amount of energy input per mole of injected gas and is described as:

$$SEI = \frac{(\nu U_{pulse} + \dot{Q}_{heat})(RT_{gas})}{\dot{V}p},$$
(6.2)

where R is the universal gas constant, \dot{V} is the volumetric flow rate and p is the pressure. The thermal power input, \dot{Q}_{heat} , is a function of the change in reactant temperature ($\Delta T_h = T_i - 300$), the mass flow rate (\dot{m}) and the heat capacity of the mixture (C_p). It characterizes the energy input delivered as gas heating and is computed by the following expression:

$$\dot{Q}_{\text{heat}} = C_p \dot{m} \Delta T_{\text{h}}.$$
 (6.3)

Figure 6.8 shows the average relative intensity of the strongest peak of $C_2(A^3\Pi - X^3\Pi)$ and $CH(A^2\Delta - X^2\Pi)$ taken near the electrodes (x = 0 mm and x = 5 mm) as a function of SEI. Increasing T_i and ν lead to similar contributions in the SEI but increasing the pulsing frequency shows a stronger effect on the intensity of $C_2(A^3\Pi - X^3\Pi)$, up to a maximum intensity ratio of 3:1 for CH_4 and CH_4 -air plasmas and 2:1 for CH_4 - CO_2 mixtures. For discharges with $\nu =$ 10 kHz and increasing U_{pulse} , emission is clearly dominated by $C_2(A^3\Pi - X^3\Pi)$, which reaches an emission intensity ratio that exceeds 10:1 for CH_4 and CH_4 - CO_2 plasmas. These findings are confirmed visually, as the discharge is completely green. The results show that $C_2(A^3\Pi - X^3\Pi)$ emission becomes dominant as more energy is delivered by the discharge and not as gas heating, suggesting that more energetic discharges lead to higher degrees of CH_4 dehydrogenation.



Figure 6.8: Relative intensity between the strongest peaks of the $C_2(A^3\Pi - X^3\Pi)$ and $CH(A^2\Delta - X^2\Pi)$ bands as a function of SEI.

6.4.3 Conversion

Gas chromatography measurements revealed the presence of H₂, C₂H₂, C₂H₄, C₂H₆, CO, CO₂ and CH₄ in the products. C₂H₂, and C₂H₄ were present in low concentrations and are not reported in this paper. Figure 6.9 shows the mole fractions of the main components of the reforming products. For $\nu = 1$ kHz, production of H₂ and CO is low, typically less than 1 %. The maximum values for H₂ and CO obtained by these experiments are 2.9 % and 1.6 %, respectively with CH₄-air mixtures at $T_i = 700$ K. For $\nu > 1$ kHz experiments, there is a clear increase in H₂ and CO production as SEI increases. The maximum H₂ amounts obtained are 29.7 %, 24.8 % and 17.7 % for pure CH₄, CH₄-air and CH₄-CO₂ respectively, all in experiments with high U_{pulse} at $\nu = 10$ kHz. This is in contrast with C₂H₆, which remains practically constant for all experiments and gas mixtures. The content of C₂H₆ remained close to 3 %, 0.9 % and 1.2 % for pure CH₄, CH₄-air and CH₄-CO₂, respectively.

The highest H_2 content is seen in products of pure CH_4 plasma. However this can be misleading, as the other two mixtures are diluted by air and CO_2 , and the maximum amount of H_2 obtainable is twice the amount of the injected CH_4 . The conversion efficiency (CE) is independent of the reactant or product composition and measures the amount of reactant that is affected by the discharge. It is the ratio of moles of converted reactant to the number of moles of reactant introduced, and it is calculated using the following expression:

$$CE = \frac{n_{CH_4}^{i} - n_{CH_4}^{o}}{n_{CH_4}^{i}} \times 100.$$
(6.4)

where n° and n^{i} are the output and input number of moles, respectively. Figure 6.10 shows CE as a function of SEI. For experiments with $\nu = 1$ kHz, increasing T_{i} does not affect CE, remaining between 5.6 to 8.9 %. Higher values of U_{pulse} produce higher CE up to a maximum



Figure 6.9: Resulting H_2 , C_2H_6 and CO mole fractions for each gas mixture as a function of SEI.



Figure 6.10: Conversion efficiency of the discharge for each gas mixture as a function of SEI.

of 18.1 % at $T_i = 700$ K and 14.3 % at $T_i = 300$ K for CH₄-air. This is not observed in pure CH₄ or CH₄-CO₂. With $\nu = 10$ kHz, the maximum values of CE achieved are 38.0 % for pure CH₄, 68.2 % for CH₄-air and 48.0 % for CH₄-CO₂. These results are similar to the intensity ratios shown in Figure 6.8, reinforcing the correlation between C₂(A³Π-X³Π) emission and CH₄ dehydrogenation and reforming. Figure 6.10 also shows a linear fit for increasing ν at $T_i = 300$ K and increasing U_{pulse} at $T_i = 700$ K and $\nu = 1$ kHz as a black and grey line, respectively. The slope of this line conveys the change in CE per kJ·mol⁻¹ applied to the gas, and it is a good indicator of the performance enhancement given by increasing the energy input. The slopes for CH₄, CH₄-air and CH₄-CO₂ are 0.11, 0.53 and 0.19 %·mol·kJ⁻¹ for increasing ν , and 0.03, 0.28, 0.02 %·mol·kJ⁻¹ for increasing U_{pulse} . Larger slopes mean higher values of CE for the same increment in specific energy input. It is clear that in terms of performance, increases, more molecules are affected per unit of gas residence time and there is less time for excited species to relax. This suggests that both time-scales have a greater effect on reforming than the energy delivered by the discharge.

At 10 kHz, increasing the energy per pulse produces a stronger effect. For pure CH_4 and CH_4-CO_2 discharges, the slopes for increasing energy per pulse are similar to the slopes for

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increasing pulse repetition frequency. This result suggests that as frequency is increased, the amount of energy delivered by the pulse becomes more relevant. It is hypothesized that the more powerful pulses are able to produce or dissociate excited species with shorter lifetimes, that would otherwise be lost at lower repetition frequencies.

A mass balance results in missing C species as SEI increases as seen in Figure 6.11 (left). This is a result of complex hydrocarbon chains that remain in the reactor as solid or liquid residues. In oxidative mixtures, a brown film is prevalent at high SEI, suggesting some degree of plasma polymerization on the quartz surface. For pure CH_4 discharges, a noticeable carbon growth appeared on the anode. Figure 6.11 (right) shows one carbon fiber glowing red with a discharge attached to the tip. The discharge can continue to operate as the fiber grows, showing that this discharge and configuration could lead to a carbon sequestration process.



Figure 6.11: Missing carbon in all experiments with respect to SEI (left) and digital photograph of a CH4 plasma at 10 kHz during the carbon build up phase (right).

The selectivity of each species gives more information on the efficiency of the discharge at producing specific molecules. Defined as the amount of a certain species produced from the

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total amount of converted reactant, it is mathematically expressed as:

$$S_{\rm H_2} = \frac{0.5n_{\rm H_2}^{\rm o}}{n_{\rm CH_4}^{\rm i} - n_{\rm CH_4}^{\rm o}} \times 100, \tag{6.5}$$

$$S_{\rm C2H6} = \frac{2n_{\rm C2H6}^{\circ}}{n_{\rm CH_4}^{\rm i} - n_{\rm CH_4}^{\circ} + n_{\rm CO_2}^{\rm i} - n_{\rm CO_2}^{\circ}} \times 100, \tag{6.6}$$

$$S_{\rm CO} = \frac{n_{\rm CO}^{\rm o}}{n_{\rm CH_4}^{\rm i} - n_{\rm CH_4}^{\rm o} + n_{\rm CO_2}^{\rm i} - n_{\rm CO_2}^{\rm o}} \times 100, \tag{6.7}$$

Figure 6.12 show the selectivities for the three main components in the products. $S_{\rm H_2}$ has similar trends as the mole fractions of products. Experiments with $\nu = 1$ kHz lead to low $S_{\rm H_2}$, except for CH₄-air discharges at $T_i = 700$ K, reaching up to a value of 25.5 %. Following similar trends as product mole fractions, higher values of ν lead to higher $S_{\rm H_2}$. Also, in this regard, oxidative mixtures have a higher $S_{\rm H_2}$ than pure CH₄, reaching a plateau close to 50 % for $\nu = 10$ kHz. The results for $S_{\rm CO}$ are similar to $S_{\rm H_2}$, with a plateau at 40 %. The value of $S_{\rm C_2H_6}$ is unexpectedly high, at 96% and 80% for $\nu = 1$ kHz discharges in pure CH₄ and oxidative mixtures, respectively. Changes in T_i seem to have no effect on $S_{\rm C_2H_6}$, remaining practically constant from 300 to 700 K. On the contrary, $S_{\rm C_2H_6}$ appears to be strongly correlated with both ν and $U_{\rm pulse}$. For increments in either parameter, $S_{\rm C_2H_6}$ is reduced until a minimum value of 8.0, 2.5 and 3.5 % for CH₄, CH₄-air and CH₄-CO₂ discharges, respectively.

For pure CH₄ plasmas, the route to hydrogen production is the dehydrogenation of CH₄ via electron impact. This is an energy intensive process, requiring energy for each step from CH₄ to C via CH₃, CH₂ and CH [174]. The amount of energy delivered into the discharge dictates how much of each of these radicals is produced. For pure CH₄ experiments with $\nu = 1$ kHz, the energy input is low, and may only be enough to produce CH₃ radicals without continuing the dehydrogenation process. CH₃ radicals react with themselves increasing the amount of C₂H₆ production. In fact, this is the reaction with the fastest rate of all C1 related reactions [95].


Figure 6.12: Selectivity of H₂, C₂H₆ and CO for each gas mixture as a function of SEI.

Moreover, CH_2 radicals can react with CH_4 enhancing C_2H_6 production. This could explain the large $S_{C_2H_6}$ for low SEI and its reduction for higher SEI. In oxidative mixtures other competing reactions take place, which may explain why, although $S_{C_2H_6}$ is high, it is lower than for pure CH_4 .

The energy efficiency is the ratio of chemical energy output contained in hydrogen and carbon monoxide products to the energy input given by the input fuel (CH₄), discharge, and heating energy. It is determined using the LHV and mass (m) of energy-containing molecules in both reactants and products, U_{pulse} , and the amount of energy Q_{heat} used to heat the gas up to T_i , calculated with Equation 6.3 multiplied by the residence time. The expression used is the following:

$$\eta = \frac{\sum (\text{LHV}_{\text{prod}} \cdot m_{\text{prod}})}{U_{\text{pulse}} + Q_{\text{heat}} + \text{LHV}_{\text{CH}_4} \cdot m_{\text{CH}_4}} \times 100.$$
(6.8)

It should be noted that as SEI increases, there are more solid and liquid residues in the products that cannot be accounted for. These have a considerably high amount of chemical energy, which results in an underestimation of the process efficiency. In this paper we consider only the major gaseous products. Figure 6.13 shows the energy efficiencies as a function of SEI. The graph mimics the conversion efficiency in practically all experiments. Low efficiency experiments had a baseline between 4.8 and 5.5%. The highest efficiencies were measured for experiments at 10 kHz resulting in 16.1% for CH₄, 25.6% for CH₄—air and 24.0% for CH₄—CO₂. Pure CH₄ conversion and energy efficiency results are similar to others found in the literature [30, 96]. Slopes of increasing ν and increasing U_{pulse} with respect to SEI are calculated from the black and grey lines, respectively. The values for CH₄, CH₄—air and CH₄—CO₂ are 0.16, 0.24 and 0.17%·mol·kJ⁻¹ for increasing ν , and 0.02, 0.12, 0.04%·mol·kJ⁻¹ for increasing U_{pulse} . These results confirm what is observed with CE, and show that increments in ν are preferential over increments in U_{pulse} . However, higher U_{pulse} produce an enhancement in performance while higher T_i appears to have no effect.



Figure 6.13: Energy efficiency of the discharge for each gas mixture as a function of SEI.

Mole fractions, selectivities and conversion efficiencies are very similar graphs. The results shown suggest that increasing the energy input by increasing ν produces better results than increasing the inlet gas temperature. Increasing T_i did not show an enhancement in reforming performance. This is not an intuitive result as reforming is traditionally carried out at high temperatures. However, it is hypothesized that increasing T_i might produce an increase in performance with a catalyst present or for longer residence times. In terms of plasma stability and ignition however, high temperatures are helpful. Increasing U_{pulse} increases efficiencies and product mole fractions, but at a lower rate than increasing ν . Adding energy into the system more frequently and in smaller portions leads to better reforming performance than delivering a large amount of energy with less frequency.

6.5 Conclusions

The effect of inlet gas temperature, energy per pulse and pulse repetition frequency on the conversion and energy efficiency for CH_4 reforming was studied using pin-to-plane nanosecond repetitively pulsed discharges. Electrical measurements, optical emission spectroscopy and gas chromatography were used to characterize the reforming performance of the discharge for a

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range of experimental conditions.

A new high-voltage pulser was developed, capable of delivering up to 2.47 mJ per pulse. Electrical measurements showed that, as the temperature and the frequency increased, the applied voltage and energy per pulse required to sustain a discharge decreased. Both parameters had a practically equal effect on the electrical characteristics of the discharge.

Spectroscopic measurements of N_2 were used to estimate the rotational temperature of nitrogen in the plasma. Using a translation stage, the axial temperature profile for each condition was acquired. It was found that, for low pulsing frequencies, the plasma channel had little temperature variation. Conversely, high frequencies showed a profile with a hot middle part followed by dips in temperature near the electrodes. All temperature profiles showed an increase in temperature near the cathode.

Further analysis of the acquired spectra revealed a trend on the emission intensity ratio of $C_2(A^3\Pi - X^3\Pi)$ and $CH(A^2\Delta - X^2\Pi)$. Discharges at 1 kHz were dominated by $CH(A^2\Delta - X^2\Pi)$ emission, giving a visually blue color. The profiles were U-shaped, with stronger $C_2(A^3\Pi - X^3\Pi)$ emission near the electrodes. This was in contrast with higher frequency discharges, which had an almost constant profile dominated by $C_2(A^3\Pi - X^3\Pi)$ emission. A correlation was identified between the emission intensity of $C_2(A^3\Pi - X^3\Pi)$ with respect to $CH(A^2\Delta - X^2\Pi)$ and the energy per pulse and frequency.

Gas chromatography measurements show CH_4 conversion for all cases. The main components identified were H_2 , C_2H_6 , CO and CO_2 , along with the unreacted input gases. High selectivity for C_2H_6 was observed in low-power and low-frequency discharges. A correlation with the energy per pulse and frequency was identified, and selectivity for H_2 and CO surpassed C_2H_6 for higher values of specific energy input. The conversion and energy efficiency followed similar trends, increasing for higher energy per pulse and pulsing frequencies. However,

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further analysis reveals that increasing the energy per pulse and pulsing frequency enhance the performance at different rates. Increasing pulsing frequency had greater gains in both conversion and energy efficiency than the energy per pulse up to 10 kHz. At this point, increasing energy per pulse produces a stronger effect, being similar to the effect produced by increasing the pulse repetition frequency. This is seen at reactant temperatures of both 300 and 700 K. Concerning this, a surprising result showed that, for the residence time of the reactor used, increasing reactant temperature had practically no effect on reforming performance.

This work showed the effect of the variation of the specific energy input through a change in the inlet gas temperature, energy per pulse, and pulse repetition frequency, demonstrating the capability of nanosecond pulsed discharges as fuel reformers. It also shows that increasing pulsing frequency produces better conversion and energy efficiencies when compared to other energy inputs, especially reactant temperature. With increasing temperatures, there was no noticeable effect on the reforming characteristics. It appears that any gas heating produced by the discharge up to 700 K does not contribute into increasing reforming performance, suggesting that the discharge effect is non-thermal in nature.

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7

Final Conclusion & Future Work

7.0.1 Thesis summary

The focus of this thesis was the development of reforming technologies using non-thermal plasmas produced from high-voltage NRP discharges at atmospheric pressure. The original work presented in the various chapters starts from a proof of concept using numerical modeling, meant to illustrate the capabilities of reforming technologies for low-emission combustion. Next, a methane reformer is presented, capable of producing syngas with a hydrogen content similar to what is predicted numerically. It ends with a clear path towards higher efficiency for hydrogen production by increasing the repetition rate of the pulsed plasma. This thesis can be subdivided into the following themes:

- 1. Numerical study of the applicability of hydrogen containing mixtures as a technology to increase the reactivity of fuel-air mixtures at relevant gas turbine engine conditions.
- 2. In-depth characterization of the different regimes produced by a NRP discharge at atmospheric pressure.
- 3. Analysis of the reforming performance and energy efficiency of each of the observed

regimes for the partial oxidation of methane.

- 4. Experimental evaluation of the reforming performance of a NRP discharge at atmospheric pressure at different reactant temperatures, energy per pulse, and repetition frequency.
- 5. Determination of the most efficient energy input for methane pyrolysis, partial oxidation and dry reforming.

The first theme is the numerical assessment of syngas as a fuel additive for the reactivity enhancement in low-emission conditions and for low calorific fuels at gas turbine engine conditions. Chapter 4 discusses the effect of syngas on the laminar flame speed and ignition delay times of methane and biogas. The composition of syngas is calculated using two reformers modeled as chemical equilibrium reactors. One is a simple biogas partial oxidation reactor and the other is a novel concept of using the exhaust gases of gas turbines as coreactants for methane partial oxidation. Two cases are studied in parallel: the adiabatic case in which hot syngas is cooled down to 300 K before being mixed with the fuel. After mixing with the fuel stream, an iterative algorithm determines the equivalence ratio of the mixture that will produce an adiabatic flame temperature of 1800 K. With these parameters set, the laminar flame speed and the ignition delay time are calculated using a 1-D freely propagating laminar flame and a 0-D reactor model, respectively.

The second theme is the implementation of a high-voltage nanosecond pulsed generator to produce a non-thermal plasma, and the characterization of the regimes observed for partial oxidation of methane. Using a variable inter-electrode distance reactor, two regimes were studied under different applied voltages. The first sections of Chapter 5 discuss the electrical and optical characteristics of this discharge for three different mixtures: pure methane, methane-air, and methane-oxygen. The electrical measurements presented include the qualitative study of the breakdown and regime-transition voltages that separate the diffuse and the filamentary regimes.

The energy per pulse is measured with the peak applied voltage, and a comparison is made between the diffuse and the filamentary regime. The optical characteristics obtained are used to estimate the temperature of the gas by fitting the modeled emission of the second positive system of N_2 with the acquired spectra, and the electron number density by determining the Stark broadening of the H_{α} line. Temperature and the electron number density are compared among the two regimes observed.

The third theme is the measurement of the reforming capabilities of each of the observed regimes for methane pyrolysis and partial oxidation of methane with air and pure oxygen. This is explored in the second half of Chapter 5, and continues with the experiments previously described in the second theme. Gas chromatography is used to measure the composition of the reforming products. To compare with each gas mixture and each regime, the energy per pulse is used as the independent variable. The main findings involve the percentage of methane converted and the energy efficiency of the discharge. The latter is calculated considering the chemical energy in the reactants and products and the energy deposited by the discharge.

The fourth theme is the implementation of a new high-voltage nanosecond pulsed generator capable of reaching higher repetition frequencies and shorter voltage pulses. The setup is similar, but uses a fixed inter-electrode distance of 5 mm. The variables studied are the reactant temperature, energy per pulse, and pulse repetition frequency, in an effort to determine which of them has the greatest influence over the conversion and energy efficiency. The first sections of Chapter 6 describe the characteristics of the resulting plasma while varying the aforementioned parameters. The electrical measurements presented include the voltage and current waveforms, and the variation of the peak voltage, and energy per pulse. The temperature is estimated by fitting the experimentally measured spectra to a modeled synthetic spectra. OES is also used to measure the relative intensity of the C_2 Swan bands with respect to CH emission.

The fifth theme is the comparison between the variations in reforming performance by

changing the reactant temperature, the energy per pulse and the pulse repetition frequency. The last section of Chapter 6 explores the changes in conversion and energy efficiency by measuring the composition of the products using gas chromatography. The energy inputs considered for the calculation of the efficiency are the energy per pulse and the chemical and thermal energy. A linear expression is fitted to determine the slope at which the efficiency varies with respect to the increase in the specific energy input. The slope is used to compare which parameter leads to the highest increase in efficiency as it varies.

7.0.2 Main Findings

The concept of non-thermal plasma fuel reformers as a technology to increase the reactivity of low-calorific fuels and low-emission conditions is explored in this thesis through numerical modeling and experimental work. The numerical simulations provide a proof of concept, while the experimental results show the applicability of non-thermal plasma discharges as the fuel reformers for this application. The acquired experimental data also gives insight on the characteristics of the plasma and the source of its reforming capabilities. The next sections outline and discuss the most important findings and results of each chapter.

Chapter 4

The numerically simulated reformer is capable of producing syngas by mixing exhaust gases with methane and allowing it to reach chemical equilibrium. The results are obtained without adding heat to the reactor, only driven by the chemistry of the high-temperature mixture. This means that the heat typically lost in the exhaust of gas turbine engines can be recovered and stored in the form of chemical energy by passing the gases into a reformer with methane. Exhaust gas recirculating reformers also proved to have a higher hydrogen output when compared to the biogas partial oxidation reactors. However, the reformer works with the exhaust

from methane and biogas combustion, as long as they are burned in a lean mixture.

The results show that even with more than 70 % dilution, hydrogen in syngas can affect the laminar flame speed of low calorific fuels, increasing it up to values similar to the baseline of methane or higher. Reactivity enhancement is observed even when it is assumed that all the heat contained after reforming is lost and the fuel mixture is cooled to room temperature. This implies that there is no need to separate hydrogen from syngas in order to produce the desired reactivity enhancement. No separation means no additional processes or energy are required, which results in higher efficiencies and allows the design of compact and efficient reactors.

Chapter 5

Using a NRP discharge, two stable regimes are observed: a diffuse and a filamentary regime. A qualitative characterization of the electrical measurements reveals the threshold voltages at which the discharge ignites into the diffuse regime and when it transits to the filamentary regime. It is found that mixtures with N_2 have a broader range of voltages for which the diffuse regime is stable. Further analysis of the electrical measurements shows that the pulse width of the applied voltage waveform appears constant with respect to the pulse amplitude in the filamentary regime and variable in the diffuse regime. This suggests that in the filamentary regime, all the circuit energy is delivered into the load, and the pulse width is dependent on the ability of the gas in the discharge gap to dissipate current. The filamentary regime is up to 10 times more energetic than the diffuse regime. Conversely, the voltage peak for sustaining the filamentary is 1.4 times lower than the maximum voltage achievable in the diffuse regime.

OES measurements reveal a practically constant temperature in both regimes with respect to the deposited energy per pulse. N_2 vibrational temperatures for both regimes are estimated close to 10 times higher compared to the rotational temperatures, indicating a high degree of disequilibrium. Nevertheless, the filamentary regime is hotter, suggesting a higher degree of

thermalization. It is concluded from these measurements that the filamentary regime is a warm plasma, with higher temperatures and higher degree of thermalization, but with the rotational and vibrational temperatures not in equilibrium.

In a similar characterization, the electron number density is estimated to be constant with respect to the energy per pulse. However, the filamentary regime is more than an order of magnitude denser than the diffuse regime, showing that the electron number density is strongly regime dependent.

The diffuse regime leads to no appreciable reformation. It is hypothesized that this is due to a low density of electrons with enough energy to dissociate methane through collisions. The filamentary regime has detectable conversion, which may be explained by the higher temperatures estimated for this regime. Results show that both the energy efficiency and the conversion efficiency scale linearly with the increase in energy per pulse, contrary to other properties measured. Additionally, oxidative mixtures have higher conversion and energy efficiencies, suggesting that species produced in non-thermal plasmas, such as oxygen singlet, ozone, oxygen ions, and atomic oxygen, become relevant for these mixtures. These species lead to better performance as their activation energies are lower than ground state molecular oxygen, accelerating the reaction rates.

Chapter 6

The effect of the inlet gas temperature, energy per pulse and pulse repetition frequency on the conversion and energy efficiency for methane reforming is measured using a NRP. The two regimes described in the previous chapter are observed, including a stable hybrid regime at higher temperatures. The voltage and energy per pulse have a decreasing tendency as temperature and pulse repetition frequency increase. The variation of these parameters has a very similar effect on both the energy per pulse and peak voltage. Temperature estimated

by fitting experimental to modeled spectra shows that, for a repetition frequency of 1 kHz, there are only small temperature variations. High frequencies, conversely, show profiles with high temperatures in the middle of the gap and lower temperatures closer to the electrodes. Temperatures rise again near the cathode, accompanied by evidence of electrode ablation. Additionally the relative emission of the C_2 Swan bands with respect to CH is observed to correlate with the discharge power.

Gas chromatography reveals conversion of methane in all cases. However, no significant conversion was observed for energy addition only by heating. This is a surprising result as reforming is typically driven by high-temperature processes. It is possible that the residence time in the reactor is too low to observe conversion. On the other hand, higher energy per pulse and higher pulse repetition frequency have a positive influence on the reforming characteristics, with conversion reaching up to 68 % in methane-air mixtures at the highest pulse repetition frequency and energy. Hydrogen content in the products reaches values that could produce an enhancement in the reactivity of low-calorific fuels and low-emission conditions as described in Chapter 4. In terms of efficiency, it is found that the greatest increase is obtained by increasing the pulse repetition frequency rather than the energy per pulse. This indicates that delivering energy frequently in small quantities is better than delivering it less often in larger quantities.

7.0.3 Contributions to knowledge

The numerical and experimental works presented in this dissertation led to several contributions to knowledge in the field of plasma-assisted fuel reforming. These contributions are:

 The concept of post-expansion exhaust gas recirculation and reforming. The numerical simulations demonstrate that, in a reactor that reaches chemical equilibrium, the exhaust gases from a gas turbine engine can be used to produce hydrogen containing gases if mixed with methane. The energy contained in high-temperature exhaust gases, is enough to drive the reforming reactions. With this, the energy contained in the exhaust gas can be recycled to produce valuable fuels instead of being wasted into the environment.

- 2. The numerical prediction that diluted hydrogen can be used to increase reactivity and allow low-emission operation and alternative low-calorific fuels. As syngas is added to the fuel stream, the modeled laminar flame speed increased and the ignition delay time decreased showing an increase in the reactivity of the mixture. Hydrogen content in the syngas used for these studies reaches a maximum of 30 %, while the rest are mainly diluents. Also, syngas-fuel-air mixtures show a reactivity increase even when assuming all heat from the reformer is lost. This demonstrates that even with dilution, and cooling down to room temperature, syngas can be used as an additive for the reactivity enhancement of fuel-air mixtures.
- 3. The identification and characterization of the different regimes of a nanosecond pulsed discharge for fuel reforming. The experiments provided in Chapter 5 give a thorough description of the two discharge regimes observed. A similar characterization has been done before for air [36], but this is the first time it is done for fuel reforming mixtures. Findings show that the temperature and electron number density of this discharge are regime-dependent, rather than dependent on the energy per pulse. Also, it is discovered that the diffuse regime has no significant reforming capabilities.
- 4. An analytical expression for the calculation of the stark broadening of the Balmer H_{α} line that depends on the electron temperature. The Stark broadening of the Balmer H_{α} line is widely known and characterized. However, although it is known that it is a parameter dependent on the electron temperature, to the best of the candidate's knowledge, there are no expressions that consider this effect. In this work, an expression is fit to tables which correlate the Stark broadening with the electron number density and temperature [157].
- 5. Insight on the reforming efficiency The effect of reactant temperature. It is observed

that the reactant temperature has no effect on the capabilities of the discharge to carry out methane reforming. This is not an expected result, and to the best of the candidate's knowledge, has not been reported previously in literature.

6. Insight on the reforming efficiency – The effect of increasing repetition frequency. Increasing the energy per pulse and pulse repetition frequency increased the energy and conversion efficiencies. However, it is discovered that the pulse repetition frequency has the greatest impact on these parameters. To the best of the candidate's knowledge, this comparison has not been reported previously in the literature.

In summary, two concepts are developed in this thesis: a reformer driven by the exhaust gases of a turbine, and the use of syngas as a control knob for the reactivity in combustible mixtures. Experimentally, a NRP discharge is characterized as a methane reforming technology. Two regimes are observed: diffuse and filamentary. The characterization reveals that the temperature and electron number density are dependent on the discharge regime and not on the energy per pulse. An analytical expression for the Stark has been broadening developed, based on data from tables that correlate the Stark broadening with the electron temperature and number density [157]. In terms of conversion, the diffuse regime is shown to be unable to convert methane in detectable amounts. For the filamentary regime, reactant temperature results in no effect, while the increase in pulse repetition frequency has the highest increase in energy and conversion efficiency.

7.0.4 Future work

There are some phenomena observed during the experiments and numerical simulations that are not the focus of the manuscripts and this thesis, but which can give a more thorough understanding of the overall process involved in non-thermal plasmas for methane reforming.

First, from the experiments, it is clear that the discharge reforming capabilities have a correlation with the temperature of the discharge. To gain a better understanding of the thermal and non-thermal contributions of the discharge, a more in-depth study of the emission and absorption characteristics of the discharge should be performed. Time-resolved instead of time-averaged measurements using the spectrometer with a fast ICCD camera could give insight on the evolution of excited species and temperature with time. Probing for other excited species, such as oxygen metastables, would allow the identification of key excited molecules that drive the reforming reactions inside a nanosecond pulsed plasma. Additionally, techniques like infrared absorption spectroscopy can be used to quantify reformed species like hydrogen along the discharge channel.

- Time-resolved OES measurements in the discharge channel. There might be peaks in temperature in time that are not captured by time-averaged measurements, and time-resolved OES would provide information on the evolution of temperature in the discharge channel over time, giving more accurate temperature estimations.
- 2. Two-photon absorption laser induced fluorescence (TALIF) could be used to quantify the number density of atomic oxygen. This would reveal how much of the CO_2 or O_2 is dissociating in the discharge and where. Also, it could be used as a metric of how reactive the plasma is.
- 3. Laser induced fluorescence (LIF) could be used similarly to quantify the number density of CH radicals, which is part of the dehydrogenation of methane. It could be an indicator of where and when methane is being dehydrogenated.
- 4. Infrared absorption spectroscopy could be used to measure the gas composition along the discharge channel. This could provide information on where the reforming reactions take place, since they may be limited to high-temperature or high reactivity zones. This study, coupled with the previous three, could be used to answer the question of whether

the contributions from the filamentary regime are mainly thermal or non-thermal.

5. The addition of a catalyst in the diffuse regime. It is hypothesized that the diffuse regime is unable to convert methane because it is mainly composed of vibrationally excited species and electrons with insufficient energy to cause dissociation by electron impact. A catalyst could test this hypothesis, since vibrationally excited methane will react with a transition metal going through its dehydrogenation reactions. If a catalyst coupled with the diffuse regime has conversion, then it would be likely that vibrationally excited species are present in the diffuse regime.

Second, although the concept of an exhaust gas recirculation reformer is feasible, experimental work needs to be carried out at gas turbine engine conditions. A reformer that can handle flow rates and temperatures that are typical of the exhaust of gas turbine would prove the concept for real applications. This requires a specialized setup that can be put to those conditions, which is likely an expensive and time consuming task.

- Increasing the reactant flow rate. For gas turbine engines, flow rates are orders of magnitude higher than what is presented in this work. The study of higher flow rates would provide insight on the feasibility of scaling a single NRP discharge for real applications.
- 2. Study an array of plasma sources. To keep the flow rate in the range studied in this work, another solution is to have multiple plasma sources acting at the same time. It is unclear if it is possible to drive an array with a single pulser or how its efficiency varies. Follow-up work to answer these questions would further demonstrate the scalability of this technology.

Finally, the reforming technology presented in this work is capable of producing syngas with up to 30 % hydrogen. This is a similar value compared to those values obtained with the

modeled exhaust gas recirculation reformer. The experimental reformer can be used to validate the numerical solutions that are presented in Chapter 4 and to determine experimentally the laminar flame speed. The experiment would entail attaching the plasma source to the fuel line and doing particle image velocimetry of the resulting flame. Precise measurements of the laminar flame speed, while the plasma source produces hydrogen, would demonstrate the concept of using plasma activation as a "reactivity knob." The above recommendations would provide a better understanding of NRP discharges for methane reforming and their applicability as reactivity modifiers in real gas turbine engines.

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