FUNDAMENTAL STUDIES ON THE EFFECTS OF CATALYST ON ATMOSPHERIC PRESSURE PLASMAS FOR AMMONIA PRODUCTION

A Dissertation

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Abstract

by

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Plasma-catalysis is a field with great potential in many applications. These include carbon dioxide (CO₂) conversion, hydrocarbon reforming, synthesis of nanomaterials, abatement of toxic waste gases, and ammonia (NH₃) production. It has several advantages: operating close to atmospheric conditions (e.g. pilot plants) unlike thermal catalysis, and not requiring a constant power supply to operate, meaning renewable energies are good candidates to power these applications. This work focuses on one of its applications, NH₃ production. Ammonia is essential for life because it is a required precursor to fertilizers, explosives, and other products. Its production represents 1-2% of energy consumption around the world. In order to improve plasma-catalysis, it is necessary to have a better understanding of the fundamental mechanisms behind catalytically-enhanced plasma ammonia synthesis, in particular, the mutual interaction between the plasma and catalyst. The literature has extensively reported plasma-catalysis manifests in an improvement of the performance of reaction kinetics when plasma and catalyst work together. These interactions between plasma and catalyst can be
interpreted from two perspectives: the effects of plasma on the catalyst and the effects of catalyst on the plasma. This work focuses on the latter, with the goal of understanding the fundamental mechanism of the plasma/catalytic synergy in NH₃ synthesis. Using a packed-bed dielectric barrier discharge, the macroscopic dielectric barrier discharge (DBD) properties were obtained using different techniques such as optical emission spectroscopy (OES), current-voltage (I-V) measurements, and charge-voltage (Q-V) measurements. It was found that there are no important statistical differences (through ANOVA analysis) between all analyzed metal-on-oxide support configurations (regardless of metal) for the filamentary characteristics (e.g. number of filaments) and nitrogen temperatures (e.g. vibrational temperature) of various excited species. These results show that the plasma is not appreciably altered by the metal catalyst even though the ammonia rate for each set of experimental conditions changed with the catalyst. Ultimately, this work shows any synergy that occurs during ammonia synthesis in this plasma-catalyst system is not due to catalyst modification of the plasma at a macroscopic level.
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CHAPTER 1:
INTRODUCTION

Plasma-catalysis is an emerging field that has the potential to disrupt a variety of industries by challenging existing technologies in environmental and energy applications (Figure 1.1). These include carbon dioxide (CO\textsubscript{2}) conversion, hydrocarbon reforming, synthesis of nanomaterials, abatement of toxic waste gases, and ammonia (NH\textsubscript{3}) production [1,2]. Conceptually, catalysis is an increase in the formation of a product by promoting a different reaction pathway due to the participation of an additional substance, called a catalyst [3]. In a historical context, the first observation of catalysis was reported by Doreiner in 1823 with his invention called Döbereiner's lamp or “tinderbox”, a lighter which used a platinum sponge as a catalyst [4]. However, the concept of catalysis was established one decade later (1835) by Berzelius, and a formal definition in terms of chemical kinetics by Ostwald in 1900 [4]. Plasma science is an old field as well. The first gas discharge was created by Hauksbee in 1705, and the first industrial device for producing ozone was invented in 1857 by Siemens [4]. The history of plasma-catalysis is relatively new, with likely the first reported observation of plasma-catalysis in 1954 by Devins et al. [5,6] in their study of the decomposition of ammonia in a direct current (DC) electric discharge. A couple of decades later, specifically in 1992, the first study using atmospheric pressure plasma, like that used in this work, for the synthesis of methanol was reported by Mizuno et al [6,7].
A non-thermal plasma (NTP) (also called a non-equilibrium plasma) is a collection of electrons, ions, and neutral gas in which the population of electrons and ions is much less than the gas. The degree of ionization, the percentage of gas that is ionized, is less than 1% [8]. The average electron energy (called the electron temperature) in a NTP is several orders of magnitude higher than the temperature of ions and neutrals ($T_{\text{gas}} \sim T_{\text{ion}} \sim 10^2 \text{K}; T_{\text{elec}} \sim 10^4 \text{K}$) [9]. The difference in the temperatures between different species in the plasma contrasts with thermal catalysis, in which all the species of the reactants (i.e., gas) are at the same temperature. The far-from-equilibrium state makes the plasma a highly reactive medium in which different types of excited species coexist at low gas temperature. For instance, in a nitrogen (N$_2$) plasma, since N$_2$ is a diatomic molecule, electronically, vibrationally and rotationally excited species can be found.
particular, the vibrationally excited species are important species in plasma-catalysis, because they may strongly influence the plasma-surface interactions.

The combination of NTPs and heterogeneous catalysis, wherein the catalyst is not in the same phase as the reactants, has attracted increased attention because of synergistic effects between a thermal catalyst and pure plasma [4]. However, there is a lack of understanding about the fundamental mechanism(s) that lead to this synergy, in particular, the mutual interactions between the plasma and catalyst. These interactions can be interpreted from two perspectives: the effects of plasma on the catalyst and the effects of catalyst on the plasma [10]. A summary with the possible synergistic effects of these two perspectives can be found in the Figure 1.2. Among the effects of the first case, we can find higher absorption probability on catalyst, higher catalyst surface area, and lowering of the activation barrier. In contrast, the effects of catalyst on plasma include electric field enhancement, change in discharge type, and micro-discharge in pores, to name a few [6,10]. As an example of change in the type of discharge, numerous publications [11–13] have shown the transition from fully filamentary discharge (no catalyst) to surface discharge along the catalyst surface due to the introduction of a catalyst.
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1.1 Ammonia Synthesis - History and Relevance

Nitrogen fixation is a natural and industrial process in which nitrogen is converted into more-reactive nitrogen compounds such as NH₃, nitrates, or nitrites [14]. Figure 1.3 shows a timeline with the milestones in the evolution of the nitrogen fixation industry. In 1903, Birkeland and Eyde invented the Birkeland-Eyde (BE) process, one of the first industrial processes for the fixation of nitrogen into nitric acid (HNO₃) [15]. The first step of this process uses an electric arc plasma system using two coaxial electrodes to convert N₂ and oxygen (O₂) into nitric oxide (NO) [1].
Figure 1.3: Timeline with the milestones of the nitrogen fixation process based on [14].

A couple of years later (Figure 1.3), the gold standard process for nitrogen fixation was invented: the Haber Bosch (H-B) process. Because of its improved energy efficiency, the HB process soon replaced BE process [1]. The H-B process exothermically converts nitrogen (N$_2$) and hydrogen (H$_2$) into ammonia (NH$_3$), and is described by the overall equation:

$$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$$  \hspace{1cm} (1.1)

Ammonia is essential to all life on our planet and its production represents approximately 1-2% of all energy consumption in the world [14,16]. The H-B process uses thermal catalysis operating under high temperature (~700 K) and high pressure (~100 atm). The dissociative absorption of N$_2$, which is the rate limiting step in the
catalytic process, occurs slowly at temperatures below 700 K [17]. This process has been extremely well optimized, and currently, there is no practical way to improve it.

Plasma-catalysis offers a good alternative with the advantage of operating close to atmospheric conditions. This is because the plasma activates stable molecules (e.g. CO$_2$ or N$_2$). In the plasma, the applied electric field will selectively heat the electrons due to their small mass, and these energetic electrons will collide with the gas molecules causing excitation, ionization, and dissociation [18]. Additionally, the introduction of a catalyst material into the reactor will enhance the electric field near the contact points of the packed bed, and thus the electron energy [18,19]. Higher energy electrons will further facilitate the activation of the gas molecules, and so improve energy efficiency. The energy yield for plasma-catalysis (~25-30 g of NH$_3$/kWh) still has poor performance compared to the H-B process (~500 g of NH$_3$/kWh) [1,18]. A better understanding of the fundamental mechanisms at work in catalytically-enhanced plasma ammonia synthesis would help to improve this. In particular, understanding the synergy between plasmas and catalysts is critical.

Finally, it is likely impossible that plasma-catalysis will compete with H-B process. However, plasma-catalysis has a great potential for modular, small scale reactors since these systems can be easily switch on/off, and therefore, renewables energies (e.g. solar or wind energy) are excellent candidates as input energies [18].

1.2 Summary of Research

This work focuses on the effects of catalysts on plasma, with the goal of understanding the fundamental mechanism of the plasma/catalytic synergy in NH$_3$
synthesis through an experimental study. Such studies have been done previously. For instance, in 2004, Mizushima et al. [17] found that the introduction of alumina or Ru/alumina into a dielectric barrier discharge (DBD) reactor increased the NH₃ yield, but neither material modified the plasma conditions. However, this study was not sufficiently systematic to draw a definite conclusion, having neither electrical nor optical measurements.

This work studies plasma/catalytic synergy using a laboratory-scale packed bed dielectric barrier discharge (DBD) to investigate the effects of different combinations of catalyst on the plasma.

The DBD plasma is produced by an alternating current (AC) power supply. There is a barrier material (e.g. quartz glass) between two electrodes in order to limit the amount of charge and therefore, the amount of current for every half cycle in which the plasma is on, preventing a transition into a thermal regime [18,20]. Figure 1.4 presents a schematic of a coaxial DBD reactor used in this work. This type of configuration is useful for testing various catalyst materials. Also, a DBD operates at atmospheric conditions, which is beneficial for certain industrial applications [18].
Two different experimental techniques are employed for the characterization of the plasma: optical emission spectroscopy (OES) and electrical characterization. Using the former one can estimate the temperature and population of various excited species at different energy levels. However, in general, there is a disconnect between the interpretation of these results and the performance of the reactor in terms of yield or conversion. Additionally, the filamentary discharge is characterized by the appearance of filaments not only in the plasma itself but also in the analysis of the current traces. There are many works [11,13,21,22] that report a correlation between the characteristic of these current filaments and the performance of the reactor. However, the stochastic nature of the plasma creates the need to use more sophisticated statistical analysis to draw better conclusions.

The goal of this research is to explore the effect of various types of materials used in packed beds on the plasma’s behavior and correlate the results of these more
fundamental studies with complementary studies of conversion of N\textsubscript{2} and hydrogen gas into NH\textsubscript{3}. The focus of this work can be outlined in the following two objectives:

**Objective 1:** Determine the effect of different catalyst/support on a packed bed DBD plasma by measuring the differences in plasma characteristics using optical emission spectroscopy (OES), current-voltage (I-V) measurements, and charge-voltage (Q-V) measurements.

**Objective 2:** Determine the effect of temperature on the plasma using the same techniques as in Objective 1, with an emphasis on changes in the populations of various excited species as a function of temperature.

Both objectives will be pursued with the aim of understanding the conditions that improve (or enhance) the yield of NH\textsubscript{3}.

The dissertation is organized into 6 chapters. Chapter 2 provides a background of plasma, catalysis, and the interaction of both. Chapter 3 introduces the different electrical characterization techniques for plasma used in this work and their respective measurements. Chapter 4 covers the optical emission spectroscopy measurements, starting with a description about the experimental set-up and then the results. Chapter 5 is about the last project, which is the analysis of the impact of high temperatures in a packed-bed reactor using the techniques introduced in the previous two chapters. Finally, Chapter 6 summarizes the results providing general conclusions, and an outline of potential future work.
CHAPTER 2:
BACKGROUND

2.1 Introduction

This chapter briefly reviews concepts that are required for understanding the fundamentals of plasma-catalysis. First, these two areas are discussed separately, then the history of plasma-catalysis is introduced.

2.2 Heterogeneous Catalysis

As a starting point, a chemical reaction is a process that leads to the chemical transformation of one set of chemical substances to another. Equation 2.1 shows a conventional chemical reaction, in which A and B are the reactants and AB the product. A chemical reaction can be classified as an endothermic (e.g. photosynthesis) or exothermic (e.g. H.B. for ammonia production) reaction if the reaction absorbs or releases heat, respectively.

A+B→AB \hspace{1cm} (2.1)

Catalysis is a process which increases the rate of reaction while the overall standard Gibbs energy change remains the same (energy difference between starting reactant and product is not changed) by adding a catalyst or a supported catalyst [3,4].
The catalyst itself is reactivated continuously after each reaction cycle [4]. The following is an example of a reaction scheme, where C represents the catalyst, A and B are the reactants, and AB is the product.

\[
\begin{align*}
A + C & \rightarrow AC \\
B + AC & \rightarrow ABC \\
ABC & \rightarrow AB + C
\end{align*}
\]

(2.2) \hspace{1cm} (2.3) \hspace{1cm} (2.4)

This work is focused on heterogeneous catalysis in which the phase of the catalyst (e.g. metals) different from that of the reactants (e.g. gases). Additionally, a support (e.g. alumina) is a lightly active catalytic substance which provides a high surface area to which the catalyst is affixed. The reaction coordinate diagram (Figure 2.1) demonstrates the functional role of a catalyst [23]. The catalyst initiates a different reaction pathway with a lower energy level (shown in pink) without changing the final result or the overall thermodynamics [23].
Figure 2.1: Reaction coordinate diagram based on [23].

One can draw a conclusion between the interaction of gas reactants and metal catalysts and an electrical circuit. The resistances correspond to the absorption ($R_{AD}$), surface reaction ($R_S$), and desorption ($R_D$) [3]. And the current $I$ (with units of Coulombs/s) can be interpreted as the rate of reaction. In particular, the metal catalysts on top of the support affect adsorption/desorption of the gas molecules on the surface. The adsorption is the attachment of the gas phase reactants to the surface, while desorption refers to their detachment. Adsorption, desorption, and surface reactions occur at active sites where the reactants form bonds on the catalyst’s surface [3].

These aforementioned concepts define one of the foundations of modern catalysis science, the Sabatier principle, which states that catalytic activity represents a trade-off between the ability of a catalytic material to activate and bind reactants and to release products. This trade-off leads to the well-known “volcano” type correlation between the binding energies of intermediates and overall catalytic rates. The optimum reactant adsorption energy is reflected by so-called volcano plots (an example of which is shown
in Figure 2.2) [4,24]. The volcano plot (Figure 2.2) relates the rates and the strength of bonding of an absorbate to the catalyst surface. The peak occurs because if the energy is too low the reactant will desorb from the surface, while if the energy is too high the products do not desorb from the surface and block the active sites [25]. In the case of NH\textsubscript{3} synthesis, the limiting reaction, which controls the shape of the volcano plot, is the binding of nitrogen to the catalytic surface.

![Volcano Plot](image)

Figure 2.2: Schematic representation of the Sabatier principle based on [24].

Finally, for describing the catalyst’s performance and activity, four main metrics can be used: conversion, selectivity, yield, and turnover frequency (TOF):

- **Conversion**: “the number of moles of reactant converted into products divided by the number of moles of reactant.” [4]

- **Selectivity**: “the conversion of the reactant(s) into the desired product divided by the total conversion of the reactant(s).” [4]

- **Yield**: “the number of moles of product divided by the number of moles of reactant fed.” [4]
• TOF: “the number of overall catalytic reaction per catalytic site per unit time for a fixed set of reaction conditions.” [4]

Of relevance here is how yield and TOF in heterogeneous catalysis are affected by low-temperature non-thermal plasmas.

2.3 Non-Equilibrium Plasmas at Atmospheric Pressure

A plasma is an electrically conductive collection of electrons, ions, and neutral gas molecules that can be either partially or fully ionized and is electrically neutral [8,26]. Plasmas constitute 99% of the visible universe (Figure 2.3) [26]. However, plasmas can also be made in a laboratory, which offers the possibility of using them in various relevant applications such as electronics, lasers, and fluorescent lamps, to name a few [26].

Figure 2.3: The Sun is an almost entirely ionized ball of plasma. The photo was taken in 2012 and it shows plasma rain in the sun’s atmosphere [27].

Due to plasmas’ complexity it is difficult to have a universal classification, because plasma can be produced over a wide range of pressures, electron densities, and electron temperatures [14]. Table 2.1 shows a general classification of the different type of plasmas, in which there is a distinction between high-temperature and low-temperature
plasmas. In fully ionized plasmas all the particles are in thermal equilibrium and therefore have the same average energies, *i.e.*, electron, ions, and background are at the same temperature \(T_{\text{gas}} \sim T_{\text{ions}} \sim T_e\).

Non-thermal plasmas (NTPs) have a non-equilibrium feature since species differ in (i.e. average kinetic energy), particularly electrons and the other particles (ions, atoms, and molecules) [11,28]. Most laboratory plasmas can be classified as non-thermal plasmas. Excessive gas heating is significantly suppressed in NTPs so that energy is mostly used for producing reactive species [29]. The temperature of electrons typically ranges from 10,000 K to 250,000 K (1–20 eV), while the gas and ions are at or near the ambient temperature \(T_{\text{ion}} \sim T_{\text{gas}} \sim 0.01\text{eV}\), because the applied electric field selectively heats the electrons due to their small mass [10]. The energetic electrons collide with the gas particles resulting in excitation, ionization, and dissociation. The collisions are probabilistic, and these probabilities are determined by the collision cross-section, \(\sigma(\varepsilon_e)\), which is a function of electron energy [8]. Due to this condition, even reactions that are strongly endothermic (requiring high temperatures) in the case of traditional thermal reaction can be carried out in plasma at adequately high rates at room temperature [4].
TABLE 2.1
CLASSIFICATION OF PLASMAS BASED ON [15]

<table>
<thead>
<tr>
<th>Type of Plasma</th>
<th>Low Temperature Plasma (LTP)</th>
<th>High Temperature Plasma (HTP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thermal Plasma</td>
<td>Non-Thermal Plasma</td>
</tr>
<tr>
<td>Criterion</td>
<td>$T_e ≈ T_i ≈ T \leq 2 \times 10^4$ K</td>
<td>$T_i ≈ T \approx 300$ K</td>
</tr>
<tr>
<td>Examples</td>
<td>Arc plasma at normal pressure</td>
<td>Low-pressure glow discharge, barrier discharge, corona</td>
</tr>
</tbody>
</table>

The particles of the plasma can all interact with each other creating a highly reactive environment, which in turn produces increased reactivity at surfaces in contact with the plasma [4]. Based on the degrees of freedom, these species can be excited translationally, rotationally, vibrationally, and electronically [26], with vibrationally-excited species strongly influencing plasma–surface interactions [4]. Vibrational excitation plays an important role in plasma chemistry because the electron’s energy (~ 1 eV) is mostly transferred to gases such as N$_2$, CO$_2$, CO, H$_2$, and so on, into a vibrational state [26]. Electronic excitation also can play an important role if the lifetime of the excited species is sufficiently long [26], [1]. Therefore, NTPs are typically described by electron temperature ($T_e$), a measure of the electron energy, as well as the gas’s electronic temperature ($T_{elec}$), vibrational temperature ($T_{vib}$), rotational temperature ($T_{rot}$) and translational temperature ($T_{trans}$), measures of the energy distributions of the corresponding modes [30].

A key characteristic of NTPs is their far-from-equilibrium state at relatively low gas temperatures, typically in the range 300–1000 K. This combination of reactivity, far-
from-equilibrium state, and low-temperature operation makes plasmas suitable for many complex applications, including catalysis [4]. In summary, low-temperature plasmas’ unique characteristics can excite energetic modes and activate processes at surfaces more efficiently and with more control compared to traditional thermal methods [4,10].

2.3.1 OES Applied to Plasmas

Optical emission spectroscopy (OES) is a non-invasive and easy to implement technique that measures the light emission of the plasma. Emission occurs when a particle in a higher energy quantum mechanical state relaxes to a lower one, emitting a photon.

![Energy Level Diagram](image)

**Figure 2.4:** Transition between two energy levels [31].

As it was mentioned before, in NTPs, many reactive species are produced, such as free radicals, excited species, and free electrons. These species can be characterized by different translational, rotational, vibrational, and electron temperatures, which can be obtained by performing OES measurements [32].

To perform a temperature analysis of the emission spectrum, a popular tool is the commercial program SPECAIR™. This is a widely used program for analyzing
atmospheric pressure air [33–36]. SPECAIR™ specializes in air plasma species and can model molecular transitions of \(NO, N_2, N_2^+, O_2, CN, OH, NH, C_2,\) and \(CO\) as well as the atomic lines of \(N, O,\) and \(C.\) For given user inputs of temperatures and molar fractions, SPECAIR™ will output a simulated spectrum that can be compared with experimental results [37].

The path taken by SPECAIR™ to compute the temperatures relies on a few key simplifying steps. First, SPECAIR™ assumes that the energy distributions of the species follow Maxwell-Boltzmann distribution, meaning that the population of a species at a specified electronic quantum number \((n),\) vibrational quantum number \((v),\) and rotational quantum number \((J)\) is given by [38]:

\[
f(n,v,J) = \frac{g_J e^{-\frac{\epsilon_J}{T_{rot}}} g_v e^{-\frac{\epsilon_v}{T_{vib}}} g_n e^{-\frac{\epsilon_n}{T_{elec}}}}{\sum_n \sum_v \sum_J g_J e^{-\frac{\epsilon_J}{T_{rot}}} g_v e^{-\frac{\epsilon_v}{T_{vib}}} g_n e^{-\frac{\epsilon_n}{T_{elec}}}},
\]

(2.5)

where \(\epsilon_q\) is the energy of the \(q\) excited state, and \(g_q\) is the degeneracy of the \(q\) excited state. To relate the distribution of species to intensity, SPECAIR™ makes use of the fact that intensity is the product of the number of species at the higher energy level and the probability of the transition occurring \((k),\) such that [38]

\[
I_{n,v,J} = k f(n,v,J),
\]

(2.6)

with the constant, \(k\) is calculated by SPECAIR™. Therefore, the ratio of two measured intensities can be related to the distributions [38]:

\[
\frac{I_{n,v,J}^A}{I_{m,w,K}^B} = \frac{k_{n,v,J}^A f(\epsilon_{A n,v,J})}{k_{m,w,K}^B f(\epsilon_{B m,w,K})},
\]

(2.7)
where A and B represent different transitions. Using the distribution equation, this can be written more explicitly as [38]:

\[
\frac{I_{n,v,J}^A}{I_{m,w,K}^B} = k_{n,v,J}^A \frac{k_{m,w,K}^B \sum_{n} \sum_{v} \sum_{J} e^{-\epsilon_J} e^{-\epsilon_v} e^{-\epsilon_n} e^{-\epsilon_m} e^{-\epsilon_w} e^{-\epsilon_K}}{\sum_{m} \sum_{w} \sum_{K} e^{-\epsilon_J} e^{-\epsilon_v} e^{-\epsilon_n} e^{-\epsilon_m} e^{-\epsilon_w} e^{-\epsilon_K}} \cdot (2.7)
\]

Based on this methodology, the different temperatures and their relative populations at different energy levels can be estimated. Additionally, the relevance to choose a specific electronic transition in order to reduce the number of free parameters (just \(T_{\text{rot}}\) and \(T_{\text{vib}}\)) can be demonstrated.

2.4 Plasma-Catalysis

Plasma-catalysis is a developing branch of plasma processing focused on improving catalytic reactions by the virtue of adding plasma to the reaction cycle [2,4,6,10,28]. Due to the complexity of this topic requires different disciplines such as physical chemistry, material science, nanotechnology, plasma physics, plasma chemistry, catalysis, and others.

Plasma-catalysis has some significant advantages over traditional thermal catalysis [39]. Due to reactive plasma species, such as electrons, ions, atoms, and radicals, catalysis can be enabled even at room temperature and atmospheric pressure. Hence, plasma-catalysis holds the promise of providing improved energy efficiency, decreased capital costs, and extended catalyst lifetime compared to traditional thermal methods [40–42]. This last plasma’s feature in combination with the selectivity of the
catalyst could imply that targeted compounds can be formed with high product yield and selectivity [18].

In plasma-catalysis, synergy is defined as the surplus effect of combining plasma with a catalyst, i.e., the effect of plasma-catalyst working together is greater than the sum of the individual effects of plasma and catalyst [4,6,10]. Synergy in plasma-catalysis is a compound occurrence, due to the interactions between the various plasma–catalyst processes [4,10,39,43,44]. The interaction can be divided into two parts. First, both the plasma and the catalyst, independent of each other, change the surface processes [4,6,10,45]. For example, the plasma creates an electric field and modifies the gas composition, which could deliver a variety of reactive species, ions, electrons, and photons to the surface [4,6,10,28,46]. The catalyst also decreases the activation barrier for certain reactions [4,6].

Second, the plasma and catalyst have some effect on each other’s properties. For instance, the plasma can adjust the catalyst morphology or work function, changing the catalyst’s operation. On the other hand, the dielectric constant or morphology of the catalyst can influence the electric-field distribution and the electron-energy distribution of the plasma [4,6,10].

In plasma-catalysis, the system pressure describes the difference between the operating conditions and thermal catalysis [4]. Thermal catalysis occurs at a different range of pressures: reduced pressures (e.g., the growth of nanomaterials such as carbon nanotubes or graphene) and high pressures (e.g., NH₃ production) [4]. By contrast, the trend in plasma catalysis, in contrast, is to work at atmospheric pressure. High pressures (i.e., above atmospheric pressure) at or near-room temperature cannot work in plasma-
catalysis, because all species would be thermalized due to the high-frequency gas-phase collisions [4]. Finally, low temperatures imply to use expensive vacuum systems.

2.5 Dielectric Barrier Discharges

Non-thermal plasmas achieve higher selectivity compared to thermal plasmas and so are more commonly used in technological applications [15]. Based on the power coupled into the plasma, non-thermal plasma can be found in different atmospheric pressure discharges, including pulsed corona, pulsed glow discharge, micro-hollow cathode discharge, dielectric barrier discharge (DBD), RF discharge, and microwave discharge [4,15].

The DBD reactor is the preferred configuration for plasma-catalysis because of its simplicity of operation [47], ease of catalyst screening, and potential for scaling [18]. Though plasma-catalysis is a developing field, DBDs have been known for more than 100 years, with first experiments reported by Siemens in 1857 [48]. Siemens generated ozone by subjecting a flow of oxygen or air to the influence of a DBD maintained in a narrow annular gap between two coaxial glass tubes [49].

DBD reactors contain two electrodes with at least one is covered by a dielectric barrier [18,49–51]. Since capacitive coupling of the dielectric requires an alternating voltage to drive a displacement current, DBDs cannot be operated with a DC voltage [49–51]. The dielectric barrier limits the amount of charge transported (or electric current), preventing the discharge from undergoing a transition into a thermal regime [18]. They are generally operated in a planar or cylindrical configuration, as shown in Figure 2.5 [51,52]. In the case of a cylindrical configuration (Figure 2.5), the discharge
gap, which is the annular discharge between cylindrical electrodes and dielectric, has a typical width ranging from less than 0.1 mm to several centimeters [49]. The required voltage to initiate the gas discharge at atmospheric pressure is in the range from a few hundred V to several kV [49].

![Diagram of DBD reactor configurations]

**Figure 2.5: Different type of DBD reactor configurations based on [51,52]**

The simplest electrical model of a DBD is the lump-element equivalent circuit as shown Figure 2.6 [48,53]. In the non-ignited case (plasma-off) the equivalent circuit is purely capacitive and consists of two capacitances, one for the dielectric barrier itself ($C_d$) (the quartz tube in this configuration) and the other the gas gap ($C_g$). Both together in series form a total capacitance $C_{cell}$ or $C_{plasma-off}$. When the plasma is ignited (plasma-on), a resistive channel appears in parallel to $C_g$. 
A Lissajous figure (Figure 2.7) shows the charge deposited in the plasma as a function of the voltage. The area enclosed by the Lissajous figure is the energy dissipated over a period. The average power (W) dissipated by the discharge is the product of the energy dissipated per cycle (the area enclosed by the Lissajous figure) and the cycle frequency. Additionally, important parameters such as the capacitances of the system can be extracted from the slopes of the Lissajous figure (Figure 2.7).

In a DBD, the discharge is ignited (plasma-on), when the applied voltage magnitude exceeds the breakdown voltage ($V_{min}$) at which the voltage reaches a certain threshold [48]. This is related to the Lissajous figure because the slopes of sides AB and CD correspond to cell or plasma-off capacitance ($C_{\text{plasma-off}}$) during the plasma-off period or “the passive or dark phases of the DBD” [11,54,55]. The slope of sides AC and BD of the Lissajous figure appears when there is a discharge (plasma-on) [11,54,55].
Figure 2.7: Physical interpretation of the Lissajous plots. (a) Dielectric barrier discharge placed in series with a capacitor. (b) Lissajous plot.

DBDs can operate at atmospheric pressure in either a filamentary or diffuse mode (if some special conditions are met) [56]. The filamentary mode is defined by a large number of microfilaments (short-lived current streamers), cylinder-like plasmas (about 100 μm radius) dispersed over the dielectric surface [11,49]. Figure 2.8 shows a schematic between Lissajous plot and current trace for a filamentary discharge at different powers. Before the breakdown voltage (Figure 2.8-a), there is a linear relation between charge and voltage (no plasma power), and no current filaments can be observed in the current traces. The diffuse mode is homogenous discharge mode without filaments. This form of DBD is also called atmospheric pressure glow because of the smooth glowing character [48]. In atmospheric pressure, the most common mode is filamentary thanks to the nature of atmospheric pressure discharges [48]. Filaments are easy to produce in a volume discharge but not in a surface discharge. In a surface
discharge, the discharge is limited in a thin layer on the dielectric surface (Figure 2.5), therefore, it is more homogeneous.

Figure 2.8: Schematic of the relation between Lissajous plot and current trace at different powers. (a) Before breakdown voltage. (b), (c), and (d) After breakdown voltage.

The introduction of particulate material in the gap between the electrodes creates a packed bed reactor (Figure 2.9). This material can have catalytic properties (supported-catalyst) to enable the selective of production of targeted compounds [10,18,45]. At the same time, the introduction of a dielectric particulate material can induce to an enhancement of the electric field near to the surface of this material, and thus a higher
electron energy [18]. The latter effect could imply a rise in the electron impact excitation, ionization, and dissociation and thus activation of the gas molecules, explaining the better energy efficiency. The introduction of a packed bed into the system may produce surface discharges along the catalyst surface as well, and the contribution of each will depend on the volume fraction of the packed material in the discharge area [11–13].

![Diagram of packed-bed reactor]

Figure 2.9: Schematic of a packed-bed reactor based on [57].

2.6 Summary

Based on the concepts introduced in this chapter, the goal of this research is to explore the effect of various types of packed beds on the plasma’s behavior using a laboratory-scale packed-bed DBD and correlate the results of these more fundamental studies with complementary studies of conversion of nitrogen and hydrogen gas into NH₃.
3.1 Introduction

Plasma-catalyst synergy manifests in an improvement of the performance of reaction-kinetics when the plasma and catalyst work together. This improvement can be explained by different interactions between plasma and catalyst, which can be simplified by the effects of plasma on catalyst and vice versa. These experiments are designed to test the latter effect: effects of the catalyst on the plasma. In particular, to investigate the possibility that the catalyst alters the macroscopic electrical properties of the plasma. For instance, larger filamentary discharges allow more energy to be deposited into the gas system, which would also aid in driving the reaction.

Therefore, in this experimental study, the effects of a catalyst on plasma capacitance and metrics obtained from filamentary discharges are investigated to determine if the macroscopic electrical changes induced by the catalyst can reasonably explain the increased ammonia yield that this configuration generates.

3.2 Ammonia Yield Measurements in a Packed Bed DBD Reactor

As a starting point, first the results of ammonia yield measurements are presented to provide context for the subsequent electrical measurements. These measurements
were conducted by collaborators Jason Hicks and Patrick Barboun and do not represent the author’s original work [58]. The experimental set-up used for ammonia yield measurements is shown in Figure 3.1. The DBD plasma was produced in a tube furnace system. The DBD plasma was driven by an AC power supply (PVM500) using a sinusoidal waveform at ~20 kHz. The reactor was made of quartz and its dimensions were 5 mm inner diameter and 7 mm outer diameter. The inner electrode was made of tungsten and its diameter was 1.5 mm. A 6 cm length stainless-steel mesh electrode (McMaster 200 × 1400 mesh) was attached to the outside of the reactor. Catalysis experiments were conducted using 100 mg of supported catalysts (metal-on-oxide) and support-only (oxide-only). When a packed bed was present, the tungsten rod was inserted through the wool (used for packing) and into the packed bed. The gas temperature was monitored with a thermocouple placed downstream from the discharge region immediately following the silica frit. Nitrogen (N\textsubscript{2}, Airgas 99.98\%) and hydrogen (H\textsubscript{2}, Airgas 99.99\%) were introduced into the system and controlled independently with mass flow controllers (Aalborg GFC17). A 10 nF capacitor was placed in series with the ground electrode. The average power dissipated by the discharge was estimated through the Lissajous figure (charge versus voltage as shown in Figure 2.7-b). As a reminder, the average power is the product of the energy dissipated per cycle (the area enclosed by the Lissajous figure) and the cycle frequency.
Figure 3.1: Schematic of the DBD packed-bed reactor used for catalyst measurements.

Reactant products were detected and quantified via in-line gas chromatography (7820A; Agilent Technologies) with a thermal conductivity detector (GC-TCD) using an Agilent CP-Volamine column. To quantify NH$_3$ production, an external calibration was performed with a commercially mixed 10% NH$_3$/He gas cylinder. For all reactions, NH$_3$ was the only product observed (that is, no hydrazine or other nitrogen-containing products were present). In some cases, due to variation in the size and shape of the metal particles, the reaction rate was normalized to the number of active surface sites for each supported-metal catalyst. The number of active metal sites was determined through carbon monoxide (CO) pulsed chemisorption using a Micromeritics ChemiSorb 2750 instrument. Additionally, a Quantachrome Nova 2200e N$_2$ physisorption instrument was used to determine the surface area of each catalyst, finding that their values are the same as previously reported.

As further motivation for this work, the site-time yield (STY) for ammonia, which is a normalized reaction rate, changed with the catalyst material as shown in Figure 3.2.
Rates vary with metal catalyst, with Co exhibiting a STY between a factor of 2 and 8 greater than Ni and Fe, respectively. These results show that the STY clearly depends on the specific metal catalyst, consistent with our findings in [59], but it is not clear that this difference in performance is due to different catalytic activity (as suggested in [59]) or if it is because they each modify the plasma itself to different degrees, changing the production of ammonia.

Figure 3.2: Measured ammonia STYs for different metal/Al₂O₃ catalysts. The reaction conditions were N₂:H₂ = 3:1, total pressure of 1 atm, plasma power of 15 W, and reactor temperature of 473 K.

3.3 Experimental Set-Up for Electrical Measurements Analysis

These measurements were conducted using the experimental set-up shown schematically in Figure 3.3, which is an equivalent configuration as used above for the rate measurements. To generate the DBD, the inner electrode, a tungsten rod of 1.5 mm diameter, was connected to an AC power supply (PVM500) producing a sinusoidal voltage at ~20 kHz and the outer electrode, a stainless-steel mesh electrode (McMaster 200 × 1400 mesh), was grounded via an external capacitor C_{ext} (10 nF) and a resistor
$R_{\text{ext}}$ (100 Ω), placed in series. The purpose of this resistor was to measure the total current using Ohm’s law ($i=V/R$). The length of the external mesh ($L_{\text{outer}}$) was varied in some experiments in order to change the discharge length relative to the packed bed length ($L_{\text{pb}}$).

![Schematic of the DBD packed-bed reactor used for electrical measurements.](image)

Figure 3.3: Schematic of the DBD packed-bed reactor used for electrical measurements.

Three different metal catalysts, iron (Fe), nickel (Ni), and cobalt (Co) (5 wt % supported on $\gamma$-alumina from Riogen Inc.) were used. A low weight-percent was used to ensure that the catalyzed reactions were kinetically limited. The support material, $\gamma$-alumina (Al$_2$O$_3$, >97; Strem Chemicals), was also used for experiments without added metal. For convenience, we abbreviate these: Al$_2$O$_3$ (support alone), Fe/Al$_2$O$_3$, Ni/Al$_2$O$_3$ and Co/Al$_2$O$_3$. The supported material and supported-catalyst material were pelletized and sieved in the particle size range of 45-90 µm, and experiments were conducted with 100 mg of supported-catalyst material in order to be consistent with our previous work [59–61]. Background measurements were conducted using Al$_2$O$_3$ only. The supported-
catalyst material was packed into the reactor and held in place by a silica frit, forming a packed bed of length of $L_{pb} \approx 1$ cm upstream of the frit.

3.4 Post-Processing Data

From the electrical analysis, two types of electrical measurements were collected: the charge deposited ($Q$) in the plasma as function of the applied voltage ($U_A$) (leading to Lissajous plots), and current ($i_T$) and voltage $U_A$ as a function of time ($t$). All the electrical signals were sampled by a four-channel high definition oscilloscope (LeCroy HDO4054A). The oscilloscope data was extracted with 12-bit resolution and a sampling rate of 2.5 GS/s. The applied voltage was measured with a high voltage probe (P6015A), and the current ($i_T$) with an oscilloscope probe (TPP0200).

The Lissajous plots consisted of using a time window of 500 μs (equivalent to approximately 10 cycles) and then averaging the resulting waveform 128 times in order to reduce the random noise. In the case of the time-dependent current, the data was collected using a time window of 200 μs, which means four negative and positive half-cycles.

3.4.1 Capacitance Data

The capacitances were obtained from Lissajous plots through a linear fitting process. To perform this, a MATLAB™ routine was implemented. The Figure 3.4 shows the nomenclature used for the calculations, in which $C_{\text{plasma-off}}^{\text{down}}$ and $C_{\text{plasma-on}}^{\text{left}}$ belong to the negative half cycle and $C_{\text{plasma-off}}^{\text{up}}$ and $C_{\text{plasma-on}}^{\text{right}}$ to the negative cycle.
Figure 3.4: Nomenclature used for the capacitance calculations.

The chosen slope value \( (C_{\text{plasma-on}} \text{ and } C_{\text{plasma-off}}) \) was selected when the coefficient of determination \( (R^2) \) was the maximized as shown in Figure 3.5. Finally, the reported capacitances were obtained by averaging the values from the positive and the negative half cycles.
Figure 3.5: Example of output data used for capacitance calculations. Panel (a): Estimated $C_{\text{plasma-off}}$ as a function of the number of data. Panel (b): Estimated $C_{\text{plasma-off}}$ as a function of the number of data. The coefficient of determination as a function of number of data is shown in panels (c) and (d) for $C_{\text{plasma-off}}$ and $C_{\text{plasma-on}}$, respectively. These values were selected when the $R^2$ was maximum.
3.4.2 Filamentary Current Data

The total current ($i_T$) in Figure 3.6 (a) is a composite current, made of a smooth oscillating displacement current ($i_D$) and the more random filamentary current ($i_P$) that occurs at the peaks of $i_D$. These currents satisfy the following relation:

$$i_T = i_D + i_P.$$  \hfill (3.1)

![Figure 3.6: (a) Total current as a function of time. (b) Fitting curve (red) to obtain the displacement curve.](image)

From Equation 3.1, $i_P$ can be extracted as $i_P = i_T - i_D$. $i_P$ was obtained using MATLAB™. First, the exact driving frequency ($f$) given by the AC power supply (PVM500) was obtained from the voltage versus time data. Then, isolating $i_D$ data from $i_T$ and using the latter parameter ($f$) for the fitting process, the best curve of $i_D$ and its amplitude ($\pm \sigma$) were obtained (red curves-Figure 3.6 (b)). Finally, the filamentary current, $i_P$, was isolated (Figure 3.7 (a)) by subtracting the displacement current from the total current.
The Savitzky-Golay (SG) filter has been used in a previous work [62] of plasma-catalysis to smooth data, with the aim of increasing the signal-to-noise ratio without greatly distorting the signal and the physics behind it. The SG filter works by fitting successive adjacent successive sub-sets of adjacent data points with a low-degree polynomial by the method of linear least squares [63]. In this work, this type of filter was evaluated to smooth data of the filamentary current. However, this filter was discarded because it clearly modified the physics as is shown in Figure 3.8. Additionally, a higher resolution oscilloscope was used in this work than in [62], and it was suitable to resolve the filament currents.
Figure 3.8: Example of Savitzky-Golay filter (red curve) applied to plasma current (black curve).

3.5 Statistical Analysis of Experimental Data

The uncertainty in the measurements was estimated using 95% confidence interval error bars and standard Student’s $t$ approaches [64,65]. In order to quantitatively assess statistical differences between any two different catalysts, a detailed statistical analysis was conducted, which is a novel method of analyzing the current in the plasma field. More specifically, the analysis of variance (ANOVA) and Tukey method technique [65] (see more details in Appendix B: ) with 0.05 significance level was performed using the software OriginPro® for each parameter in order to explore any statistical difference. One of the assumptions of the ANOVA analysis is that measurements follow a normal distribution. In order to ensure transparency in the data, plots of electrical data include both the mean with error bars (reflecting 95% confidence intervals) and scatter of the raw data.

For the electrical characterization, every measurement at a specific condition was repeated at least 4 times, and then these measurements were repeated again a second day,
which means every condition has at least 8 repetitions. The experiments for every tested material were performed on two different days, and on each day we loaded new packed bed material into the reactor. This approach was to ensure that the initial state of the packing material was the same (in case the plasma modified the material), but there could have been day-to-day variations in how well the material was inserted into the reactor, the exact placement of the inner electrode, and potentially other minor variations. For OES measurements, every measurement at a specific condition was repeated 5 times. Finally, for the measurements of ammonia rates, every condition was repeated three times for each flow rate.

3.6 Capacitance Analysis and Results

The Lissajous plots were analyzed from two different perspectives: qualitative and quantitative. As Figure 3.9 demonstrates, in the experiment with Al₂O₃ alone and with metal catalysts (Fe, Ni and Co) similar parallelogram-like shaped Lissajous plots can be observed. Qualitatively, the measurements were not different.
Figure 3.9: Lissajous plots for (a) Al$_2$O$_3$, (b) Fe/Al$_2$O$_3$, (c) Ni/Al$_2$O$_3$, (d) Co/Al$_2$O$_3$. For all these cases, the reactor was run at 15 W, a total flow rate of 40 sccm, a reactant ratio N$_2$/H$_2$=3, and $L_{pb}/L_{outer}$ ~ 1/6.

In the literature this type of shape was demonstrated for typical filamentary DBD [30]. However, using a packed bed in the system caused a small ‘hump’ in the lower part of the curve shown in Figure 3.9 and Figure 3.10. The plasma current traces illustrated in Figure 3.11 are also different with the addition of the packed bed. Hence, the packed bed has an impact on both the Lissajous plot and the filamentary behavior. Based on this the hump could be explained by the sharp increase in the current when the discharge first ignites in a positive half-cycle.
Figure 3.10: Comparison Lissajous plots: (a) 15 W DBD with 100 mg of Fe/Al$_2$O$_3$. (b) 15 W DBD alone.

Figure 3.11: Comparison plasma current traces: (a) 15 W DBD with 100 mg of Fe/Al$_2$O$_3$. (b) 15 W DBD alone.

From a quantitative point of view, the slopes of the curves were analyzed with more detail. As was previously described, the greater slopes of the curve (AC and BD in Figure 3.9) correspond to the active phase (effective capacitance of the system) when the filaments were formed and the smaller slopes (AB and CD in Figure 3.9) describe the capacitance during the inactive phase.
Figure 3.12: Extracted capacitance values for Al\(_2\)O\(_3\), Fe/Al\(_2\)O\(_3\), Ni/Al\(_2\)O\(_3\), and Co/Al\(_2\)O\(_3\) from Figure 3.9 – (a) \(C_{\text{plasma-off}}\) and (b) \(C_{\text{plasma-on}}\). The plots show scatter columns of the raw data with their respective averages and 95\% confidence interval error bars.

Figure 3.12 summarizes the capacitance properties of the different catalyst measurements. In general, the results suggest that there is no appreciable difference between the different capacitance values. The inactive phase (Figure 3.12 (a)) shows indistinguishable mean values and not greater than 5.1\% maximum difference. In the active side (Figure 3.12 (b)) there is a little more variance, however, the maximum difference between the mean values is only 6.4\%. Hence, it can be concluded that differences in the ammonia STYs shown in Figure 3.2 are not related to the effect of the catalyst on the electrical field.

As starting point, Figure 3.13 shows a proposed representative electrical circuit of a packed bed DBD reactor. In the presence of the solid catalyst in the gas gap, the capacitance \(C_{pb}\) represents the contribution of the gas–solid integration in the inter-electrode region, while the capacitance \(C_{gas}\) just the gas (N\(_2\)/H\(_2\) mixture). When the plasma is ignited, a resistive channel appears in parallel to \(C_{pb}\) and \(C_{gas}\). The switch \(K\) on
the representative electrical circuit is fictional and simply reflects plasma ignition. The equivalent capacitance of the dielectric \( C_{\text{die}} \) is calculated using the coaxial topology of a double quartz barrier [11,66].

![Diagram of electrical circuit]

**Figure 3.13:** Proposed electrical circuit of the current packed bed DBD reactor

First consider \( C_{\text{plasma-off}} \), which can be estimated theoretically using

\[
C_{\text{plasma-off}} = \left( \frac{1}{C_{\text{die}}} + \frac{1}{C_{\text{pb}} + C_{\text{gas}}} \right)^{-1}. \tag{3.2}
\]

Based on the dimensions of the quartz glass tube reactor and considering an outer electrode length of 6 cm, the equivalent capacitance of the dielectric tube \( C_{\text{die}} \) is 37.7 pF [11,66]. If we add in the packed bed of Al\(_2\)O\(_3\), the measured total pore volume is 0.4025 cm\(^3\)/g, which means that for 100 mg of Al\(_2\)O\(_3\) (equivalent to ~1 cm length in our
reactor), the porosity is ~21%. To account for the relative contributions of the Al₂O₃ and
gas portions of the packed bed, we can use the effective medium approximation [67] to
estimate an equivalent dielectric constant for the packed bed of \( \varepsilon_{\text{packed bed}} = 1.56 \),
leading to an equivalent capacitance of \( C_{pb} = 0.72 \) pF. Substituting this value into
equation (3.2), \( C_{\text{plasma-off}} \) is approximately 2.81 pF.

Now consider the addition of a Ni catalyst to produce Ni/Al₂O₃. The total pore
volume was measured to be 0.4812 cm³/g, which means that for 100 mg of Ni/Al₂O₃
(~0.6 cm length), the porosity is ~41%. The equivalent dielectric constant of the
Ni/Al₂O₃ material (assuming a very large dielectric constant for Ni) is 10.53, and the
corresponding dielectric constant of the packed bed is \( \varepsilon_{\text{packed bed}} = 2.31 \), leading to a
capacitance of \( C_{\text{packed bed}} = 0.64 \) pF. Finally, substituting these values into Equation
3.2, \( C_{\text{plasma-off}} \) for Ni/Al₂O₃ is 2.9 pF, only 3% higher in comparison with \( C_{\text{plasma-off}} \)
for just Al₂O₃ in the reactor. While our measured values of \( C_{\text{plasma-off}} \) in Figure 3.12
are slightly higher than these estimates, it is clear that it is not unexpected that the metal
catalysts had little effect on the capacitance.

When the plasma is on, the value of the capacitance is usually similar to the
capacitance of the dielectric itself \( (C_{\text{plasma-on}} \sim C_{\text{die}}) \), assuming that the plasma itself is
purely resistive and not capacitive [48]. In this case, we see that the measured \( C_{\text{plasma-on}} \)
value of approximately 33 pF in all cases is lower than the analytically predicted value of
37.7 pF, so there may be a small capacitive component to the discharge. If that is the
case, however, we would expect the same impact of the metal material as we discuss
above, and thus again it is not surprising that there are no clear, statistically
distinguishable differences.

3.7 Filamentary Current Analysis

For the filamentary current analysis four different metrics were used in order to
characterize the filamentary behavior with the presence of different catalysts: the time-
averaged filamentary current ($I_f$), number of filaments in a given half-cycle ($N_f$), the
average filament magnitude (i.e., peak height, $h_f$), and the lifetime of the filamentary
current ($\tau_f$). These metrics are commonly used for analyzing DBD [11] [32]. Due to the
asymmetric electrical behavior of the DBD in our configuration [12], all of the metrics
were obtained for the negative and positive cycle independently as well averaging four
cycles for each (noted as subscript “-avg” in the metrics nomenclature). The
measurements were taken with three different flow rates: 30, 40, and 50 sccm. However,
appreciable difference could not be found among the properties of the different flow rate
measurements. In this section, the results were obtained under the following experimental
conditions: For all cases, the reactor was run at 15 W, a total flow rate of 40 sccm, a
reactant ratio $N_2/H_2 = 3$, and $L_{rib}/L_{outer} \sim 1/6$. The macroscopic electrical properties for the
rest of the studied flow rates (30 sccm and 50 sccm) are contained in the Appendix D:
and they show similar behavior in comparison with 40 sccm.

As a starting point, one example of the collected current traces for the different
catalyst/support with 40 sccm flow rate is summarized in Figure 3.14.
Figure 3.14: Plasma current traces for (a) Al$_2$O$_3$, (b) Fe/Al$_2$O$_3$, (c) Ni/Al$_2$O$_3$, (d) Co/Al$_2$O$_3$.

The first metric is the time-averaged filamentary current, which is defined as:

$$I_f = \frac{2}{\tau} \int_0^{\tau/2} I_f^*(t) dt$$  \hspace{1cm} (3.3)$$

where $\tau$ is the cycle period. This parameter directly correlates to the plasma charge when multiplied by the half-period [21,68], and Oskan et al. [68] showed in their experiments for splitting of CO$_2$ that this metric is sensitive to the applied power and not to the frequency. Figure 3.15 presents the values and the ANOVA analysis for the different catalyst/support cases. There is no notable difference between the different
configurations, which is supported by the statistical analysis. This result is consistent with the findings in the case of the Lissajous plot analysis.

Importantly, the amount of current and thus charge deposited is directly related to the electron density in the discharge [69]. As all chemical processes in the plasma originate from electrons and the corresponding reaction rates depend on the electron density, these results support the conclusion that the chemical processes in the bulk of the plasma are not appreciably changed by the presence of metal catalysts. That is, the metal catalyst does not affect the chemistry of the discharge, and thus the enhanced STY in Figure 3.2 is due to some other mechanism likely occurring at the catalyst surface itself. However, caution must be exercised when using this interpretation, as this result only allows an average assessment rather than a local characterization. Furthermore, the rate constants themselves might be altered independently, and that is not a conclusion that can be drawn from this data.
Figure 3.15: Extracted time-average filamentary current per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for time-average peak current values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

The second metric is the number of filaments per half cycle ($N_f$), defined mathematically as

$$N_f = \sum_0^{T/2} N_f^*(t).$$  \hspace{5cm} (3.4)

In their work on CO$_2$ dissociation, Uytdenhouwen et al. concluded that reducing the gap size at a constant power input shows a greater number of filaments (microdischarges) that could play an important role in the conversion of CO$_2$ due to a higher reduced electric field or power density [22]. Similarly, for the reforming of CH$_4$, Brune et al., Whitehead, and co-workers observed a smaller number of filaments in the presence of metal-on-oxide support configurations in comparison with systems having just plasma [11], [11], [39], although this depended on the density of the packed bed.
Figure 3.16 demonstrates the asymmetry in the system; the positive and negative half-cycles show distinguishable difference. During the negative half-cycle there are some statistical differences, according to the ANOVA analysis. In this case no clear conclusion can be drawn since the determined differences cannot be correlated to the STY results shown in Figure 3.2. No statistical difference was found among Co/Al2O3 and Ni/Al2O3 in spite of the distinguishable difference appeared in the STYs.

The third metric is the average current of the filaments, which corresponds to the magnitude or height of the peaks in the oscillogram, and is defined as:

\[ h_f = \sum_{i=1}^{N_{t/2}} h_f(i) / N_{t/2}. \]  

(3.5)

where \( N \) is the number of filaments. A greater value of this metric would imply more intense filaments [71], which would correspond to higher electron densities and hence to
more effective NH₃ generation in the plasma itself. Figure 3.17 also reflects the asymmetric behavior since the values of the negative and positive half-cycle are clearly distinguishable. For \( h_{f-avg} \) only Fe/Al₂O₃ and Ni/Al₂O₃ show statistical difference in the positive half-cycle.

![Figure 3.17: Extracted average current of the filaments per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for average current of the filaments values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.](image)

The final metric, average lifetime of each filament, was based on analysis of the full width half maximum (FWHM), is reported in Figure 3.18. Here, there is no noticeable difference between the values of the positive and negative half-cycle, which was reported for the previously discussed variables. Also, the ANOVA analysis did not show conclusive findings with respect to the correlation between the trends observed in STYs and the apparent statistical differences.
Figure 3.18: Extracted average lifetime of each filament per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for average lifetime of each filament values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

3.8 Analysis and Verification of Findings

One weakness of these measurements is that the DBD region in our system covers much more volume than just the packed bed region of catalytic material. Also, as few of the electrical measurements showed differences that were statistically significant, it was necessary to confirm that the oscilloscope measurements at 12-bit resolution and a sampling rate of 2.5 GS/s were sufficient to resolve electrical differences. Therefore, two additional configurations – one with no packed bed and one with a packed bed of barium titanate (BaTiO₃), which has a much higher relative permittivity (~1250) than Al₂O₃ [45] were tested. For all these cases, the reactor was run at 15 W, total flow rate \( Q = 40 \) sccm, reactant ratio \( N_2/H_2 = 3 \), and \( L_{pb}/L_{outer} \sim 1/6 \). Figure 3.19 show the current traces for these three configurations. As shown in Figure 3.20, each of these configurations produced different filamentary results than a system with metal/Al₂O₃ (in this case Co/Al₂O₃),
providing a good benchmark that our experimental method and data analysis can resolve differences in configuration. Finally, Figure 3.21 shows a qualitative comparison of the Lissajous plots. The Lissajous plot for a system with BATiO₃ appears more almond-shaped than like a parallelogram.

![Plasma current traces](image)

Figure 3.19: Plasma current traces for (a) no catalyst/support, (b) Co/Al₂O₃, (c) BaTiO₃.
Figure 3.20: (a) time-average filamentary current, (b) average number of filaments (c) average current of the filaments, and (d) average lifetime of each filament values for no catalyst/support (blue circles), Co/Al$_2$O$_3$ (red circles) and BaTiO$_3$. All these metrics were evaluated over half-cycle.

Figure 3.21: Lissajous plots for (a) no catalyst/support, (b) Co/Al$_2$O$_3$, (c) BaTiO$_3$.

The second benchmark was to conduct measurements where the length of the outer electrode was also be 1 cm, such that the ratio of the supported catalyst length ($L_{pb}$) to the outer electrode length ($L_{outer}$) is effectively 1. This ensures that all of the plasma passes
through the packed bed and our measurements reflect actual interactions between the plasma and catalyst region. In order to make the comparison fair, the power in the discharge was 2.5 W in order to have the same power density.

The following figures (Figure 3.22, Figure 3.23, and Figure 3.24) were obtained under the following conditions: 2.5 W, a total flow rate of 40 sccm, a reactant ratio N₂/H₂=3, and \( \frac{L_{pb}}{L_{outer}} \sim 1 \). Notably, the qualitative characteristics of the Lissajous plots are different for \( \frac{L_{pb}}{L_{outer}} \sim 1 \) than \( \frac{L_{pb}}{L_{outer}} \sim 1/6 \), appearing more almond-shaped than like a parallelogram in Figure 3.22. We attribute this difference in the shape to the difference in a filamentary discharge for \( \frac{L_{pb}}{L_{outer}} \sim 1/6 \), to a surface discharge for \( \frac{L_{pb}}{L_{outer}} \sim 1 \), when all the discharge is through the packed bed; similar observations were reported in the work of Tu et al. when varying the density of the packed bed [16]. However, again there is no measurable difference between the different metal catalysts. This is also apparent when comparing other metrics (Figure 3.23 and Figure 3.24) with all metal catalysts producing statistically similar values (confirmed using ANOVA analysis).
Figure 3.22: Lissajous for Al$_2$O$_3$, Fe/Al$_2$O$_3$, Ni/Al$_2$O$_3$, Co/Al$_2$O$_3$ and show little variation between the different metal catalysts.

Figure 3.23: Extracted average number of filaments per half-cycle shows a little variation between the different metal catalysts. Panel (a) shows scatter columns for average number of filaments values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values. Experimental conditions: 2.5 W, 40 sccm, N$_2$/H$_2$=3, and $L_{ps}/L_{souter}$$\sim$1.
Figure 3.24: Extracted average lifetime of each filament per half-cycle shows a little variation between the different metal catalysts. Panel (a) shows scatter columns for average lifetime of each filament values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values. Experimental conditions: 2.5 W, 40 sccm, $N_2/H_2=3$, and $L_{pb}/L_{outer}=1$.

3.9 Summary of Findings

In this chapter, a packed bed DBD reactor for ammonia synthesis was studied. From our collaborator’s results, they showed different supported-catalyst provided different ammonia rates in a packed bed DBD reactor, in particular, $Co>Ni>Fe$. Based on this, the outstanding question of this chapter was if the metal catalyst modified the macroscopic electrical properties of the plasma.

Without a packed bed, the reactor operated under purely filamentary DBD behavior. However, the introduction of a packed bed implied surface discharges along the packed bed. Over the breakdown voltage, total current showed the appearance of current filaments. These current filaments could be directly characterized by subtracting out the displacement current. The dynamic of these filaments was analyzed through different metrics: time-average filamentary current, number of filaments, height of the filaments,
and filaments’ width with the final purpose to characterize the plasma itself. From a statistical analysis, ANOVA and Tukey method technique, these filaments practically did not show statistical differences among all supported catalyst configurations: Co/Al₂O₃, Ni/Al₂O₃ and, Fe/Al₂O₃. Additionally, the Lissajous plot, which is the charge deposited in the plasma as a function of voltage, were analyzed for the different configurations. Qualitative and quantitative analysis were performed, and they showed practically no difference among all studied cases. In summary, all the results introduced in this chapter supported the argument that the observed synergy in the catalysis experiments were not due to the catalyst modifying the characteristics of the plasma itself.
CHAPTER 4:

OPTICAL EMISSION SPECTROSCOPY

4.1 Introduction

Optical emission spectroscopy is a popular non-invasive technique used to characterize plasmas. This technique can be used to estimate important plasma parameters such as the electron temperature, the electron density, and the temperature of the different populations of excited species, which are at different energy levels. These excited species could play an important role in explaining the production of ammonia in near atmospheric conditions. Additionally, an enhancement of the production of ammonia was observed in the presence of packing materials (supported-catalysts) in the DBD reactor. The hypothesis of one previous work [59] was that plasma creates high populations of vibrationally-excited N\textsubscript{2} at near ambient temperatures, which dissociate more easily on the catalyst. For this reason, it was important to have a reliable methodology to evaluate the plasma’s temperatures not only of the plasma itself but also the interaction between the plasma and supported-catalyst. The latter is challenging due to the opaque nature of the supported-catalysts. However, OES measurements were also used to evaluate the effect of the different supported catalysts on the plasma.
4.2 Experimental Configurations

An Ocean Optics USB2000+ spectrometer (optical resolution 1.5 nm) was used for most of the OES measurements. Based on this resolution, it cannot distinguish the NH emission line at 336 nm [72] from the N$_2$ line at 337 nm. However, as a benchmark study, the values of N$_2$ vibrational temperatures obtained using the Ocean Optics spectrometer were compared with those from a higher resolution Andor Shamrock 303i spectrometer. The values were relatively similar (less than 5% of difference). The latter spectrometer has an optical resolution of 0.43 nm, 0.1 nm, and 0.06 nm, depending on the chosen grating [73]. In this work, an optical resolution of 0.06 mm was used.

The experimental set-up for OES measurements changed many times from its initial design. The reactor design was made to be both easily modified and consistent with the reactor that produced the ammonia yield measurements discussed in Section 3.2.

At the beginning of this project, the reactor was the one shown in Figure 4.1, which had dimensions consistent with the straight reactor used for ammonia yield measurements, which means 7 mm outer diameter and 5 mm inner diameter [60,61]. The fiber optic was installed outside of the straight reactor and perpendicular to the gas flow. Initially, experiments were performed with 100% He gas. The analysis of the spectra showed air peaks, and it was unclear if the origin of the air contamination was internal or external to discharge tube. Additionally, corona discharges were observed between the outer electrode and the metal support where the fiber optic was mounted. For these reasons, we decided to change the design.
The second system in which OES measurements were performed is presented in Figure 4.2. The DBD plasma reactor was identical to the one used in the plasma-assisted catalysis measurements, save for a small modification that allowed better optical access. As shown in Figure 4.2, the spectrometer was integrated “in-line” with the DBD plasma, such that it acquired the light emitted by the plasma down the length of the tube. This configuration was used to mitigate the impact of external discharges and other light sources on the OES measurements.
Figure 4.2: Second “in-line” configuration used for performing optical emission spectroscopy measurements.

The final system design for OES is shown in Figure 4.3. This design included a modified, L-shaped quartz reactor tube with 5 mm inner diameter and 8 mm outer diameter. The catalyst material was packed into the 90° bend where a planar quartz window was integrated into the tube to allow for emission measurements. This configuration allowed for more effective optical access to the catalyst-packed bed than the straight reactor tube configuration used for ammonia synthesis kinetic measurements. OES measurements conducted on the second and third configurations confirmed that the L-shaped geometry did not appreciably alter the quantitative data (Figure 4.4).
Figure 4.3: Final configuration used for performing optical emission spectroscopy measurements.

Figure 4.4: Comparison of the estimated vibrational temperature as a function of the composition using straight reactor “in-line” configuration (black square) and L-shape reactor (third configuration) (blue triangle).
4.3 Post-Processing the Data

A gaseous plasma can be characterized by the thermal disequilibrium \( T_e \neq T_{ex} \neq T_{vib} \neq T_{rot} \neq T_{gas} \), where \( T_e \) is the translational temperatures respectively for the free electrons and heavy species, and \( T_{ex}, T_{vib}, T_{rot} \) are the internal temperatures respectively associated with the electronic, vibrational and rotational excited states of the species in the plasma [74]. A DBD plasma is a low-temperature non-thermal plasma which obeys the following relation \( T_e > T_{vib} > T_{rot} \approx T_{gas} \). In general, this analysis focuses on the second positive system of \( \text{N}_2 \) (Figure 4.5), which produces emission lines from approximately 300-385 nm [30,75]. The electronic transition lines are due to the transition between the third and the second excited triplet states of nitrogen molecules, \( \text{i.e.} C_3\Pi_u \rightarrow B_3\Pi_g \) [30]. As a reference, Table 4.1 shows significant spectral lines in an atmospheric pressure nitrogen discharge [30,38]. The emission spectra were curve fit using the commercial software SPECAIR, which calculates the OES by determining the population of the upper state of the transitions based on a Boltzmann distribution and the specified temperatures of the internal energy modes [76]. A theoretical spectrum was produced by convolving the theoretical emission spectrum with the slit function. In the range of 300-385 nm (see example Figure 4.6), the relative intensities of roto-vibrational lines are independent of \( T_{ex} \) [77] and thus only \( T_{vib} \) and \( T_{rot} \) were used as fitting parameters.
Figure 4.5: Schematic potential energy diagram of the neutral and ionic nitrogen molecules based on [78].
TABLE 4.1
SIGNIFICANT SPECTRAL LINES IN ATM. PRESSURE NITROGEN DISCHARGE
BASED ON [30,38]

<table>
<thead>
<tr>
<th>Excited species</th>
<th>Wavelength (nm)</th>
<th>Electronic transition</th>
<th>Vibrational transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>295.2</td>
<td>N₂(CʻΠ₉₋BʻΠ₇)</td>
<td>4-2</td>
</tr>
<tr>
<td>N₂</td>
<td>296.1</td>
<td>N₂(CʻΠ₉₋BʻΠ₇)</td>
<td>3-1</td>
</tr>
<tr>
<td>N₂</td>
<td>297.5</td>
<td>N₂(CʻΠ₉₋BʻΠ₇)</td>
<td>2-0</td>
</tr>
<tr>
<td>N₂</td>
<td>311.5</td>
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Figure 4.6: Example of fitting experimental spectrum using SPECAIR\textsuperscript{TM}.

The slit function is a critical input for post processing data with SPECAIR\textsuperscript{TM}. The slit function is the representation of the instrument (spectrometer) response and its broadening depends on the slit width, pixel width, and grating dispersion. In the absence of the slit function, the emission spectrum contains many very sharp lines (such as the blue line in Figure 4.7-b). These peaks consider only Doppler, collisional, and natural broadening. By convolving with the slit function, the experimental spectrum can be recovered (red line, Figure 4.7-b). The slit function (Figure 4.7-a) was measured using a diode laser (Thorlabs) at 635 nm with the Ocean Optics USB 2000+ spectrometer.

However, an alternative method involves fitting the data as well as possible and then changing the slit function manually until the optimal results are reached. Typically, a triangle or trapezoid slit function is sufficient for this purpose. This methodology was used to choose the slit function for the Andor Shamrock 303i spectrometer. In this case, the slit function was a trapezoid of base 0.36 nm and top 0.18 nm [79].
4.4 Vibrational Temperature as Function of Gas Composition

In thermal catalysis (Haber-Bosch process), it is believed that the rate limiting step is the dissociative absorption of N$_2$ [3,80]. Metha et al. [59] postulated that the plasma creates high populations of vibrationally-excited N$_2$ species at near ambient temperatures, which dissociate more easily on the catalyst. The dissociation of vibrationally-excited nitrogen was incorporated in a microkinetic model, which predicted that it is possible to produce NH$_3$ at low temperatures and atmospheric pressure in plasma-catalytic reaction environments at rates that can match those of the high temperature and pressure Haber-Bosch process [59].

The effect of the N$_2$ vibrationally excitation was hypothesized for a reduction of the energy barrier described by Equation 4.2 [59]:

$$k^{(f)}_v = A \exp \left(-\frac{E_a - \alpha E_v}{k_B T} \right)$$

(4.2)

And so, the rate was written as follows [59]:

---

Figure 4.7: Slit function measured using a diode laser (Thorlabs) at 625 nm with Ocean Optics USB 2000+ spectrometer.
\[ r_1(v) = k_v^{(f)} p_v N_2 \theta_v^2 - k_v^{(b)} \frac{\theta_v^2}{\theta_N^2} \]  

(4.3)

Here, the N\textsubscript{2} vibrationally-excited population was expressed using a non-Boltzmann distribution, called the Treanor formula (Equation 4.4) [26,59,81]. The Treanor formula takes into vibrational-vibrational energy transfer mechanism that results in the overpopulation of higher-energy vibrational levels [26,59]. Also, it assumes absence of the process transferring vibrational energy into the translational degree of freedom, in other words, into gas heating under molecule collisions [81].

\[ p_v(v, T_{vib}, T_{gas}) = B \exp \left( -\frac{h \omega v}{T_{vib}} + \frac{x_c h \omega v^2}{T_{gas}} \right) \]  

(4.4)

Figure 4.8: Comparison of Boltzmann distribution versus Treanor distribution.

As mentioned before, the N\textsubscript{2} vibrationally-excited population was estimated by measuring the N\textsubscript{2} vibrational temperature. OES measurements were performed with this purpose. Measurements were conducted in pure N\textsubscript{2} and H\textsubscript{2} at a fixed total flow rate of 20 sccm with the flow ratio of N\textsubscript{2}/H\textsubscript{2} varying from 0.33 to 5.0. In particular, three
Experimental conditions were tested: 10 W DBD plasma with no catalyst material, a 10 W DBD plasma with 100 mg Al₂O₃ support, and a 10 W DBD plasma with 100 mg Al₂O₃ support and 5% Ni catalyst. The average plasma power ($P$) was found by averaging the instantaneous power over one cycle ($\tau$):

$$\bar{P} = \frac{\int_\tau^\tau (v(t)i(t) - i(t)^2 R) dt}{\tau}$$  \hspace{1cm} (4.5)

An optical fiber connected to an Ocean Optics USB2000+ spectrometer recorded emission data. In the configuration with no catalyst, an integration time of 0.01 s was employed, while in the configurations with either a 100 mg Al₂O₃ support or a 100 mg Al₂O₃ support mixed with 5% Ni catalyst, an integration time of 0.05 s was used. Figure 4.9 shows an example for emission spectra at 10 W and flow rate for 20 sccm for different N₂/H₂ ratios for all studied configurations. For the analysis, it was assumed that the rotational and translational temperatures were approximately equal ($T_{rot} \approx T_{gas}$) due to the fast relaxation time of the rotational states [30,76,77,82]. An example of the experimental fitting is shown in Figure 4.10.
Figure 4.9: Emission spectra of a 10 W DBD for different N$_2$/H$_2$ ratios at a total flow rate of 20 sccm: (a) DBD, (b) DBD/Al$_2$O$_3$, and (c) DBD/Ni/Al$_2$O$_3$. 
4.4.1 Findings

Figure 4.11 shows the results obtained for this work [59]. Error bars indicate a 95% confidence interval. The estimated N$_2$ vibrational temperature decreases with increasing the N$_2$ content but it had a weak dependence on the gas composition. Similar trend was observed in a previous work [83] of OES measurements for N$_2$ discharge. Additionally, the introduction of a catalyst (Ni) in the N$_2$/H$_2$ discharge increased the vibrational temperature of N$_2$ suggesting that plasma-catalysis system shifts the electron energy distribution towards rich electrons in the high-energy tail of the distribution function [13]. In a similar way, Tu et al [13] showed same trend with the presence of TiO$_2$ in a N$_2$ DBD.
4.5 Vibrational Temperature as Function of Catalyst Material

Based on previous work [59], it was argued that plasmas create high populations of vibrationally-excited $N_2$ at near-ambient temperatures, which dissociate more easily on the catalyst due to a reduction in the activation energy. Following the same line of thought, Patil postulated that for plasma-based nitric oxide (NO) synthesis (without a catalyst) the vibrational and electronic excitation of $N_2$ molecules promotes the gas-phase dissociation process [15], where vibrational excitation is the most energy efficient channel in non-thermal plasma [26]. When considering the effect of metal catalysts on the plasma, a significant change in the vibrational temperature would suggest a modified electron energy distribution [13], which may correlate to more (or less) $N_2$ dissociation in the plasma itself.

OES measurements were performed in order to characterize thermodynamic properties in the plasma, and to test if the metal catalyst modifies the plasma properties.
In particular, we wanted to see if these modifications played a role in different ammonia synthesis rates for different metal catalysts. With this purpose, measurements were conducted in pure N\textsubscript{2} and H\textsubscript{2} at a fixed total flow rate of 40 sccm and fixed flow ratio (N\textsubscript{2}/H\textsubscript{2}=3). In particular, all the experiments were performed at 15 W, and four packed-bed materials were tested: 100 mg Al\textsubscript{2}O\textsubscript{3} support, 100 mg Al\textsubscript{2}O\textsubscript{3} support and 5% Fe catalyst, 100 mg Al\textsubscript{2}O\textsubscript{3} support and 5% Ni catalyst, and 100 mg Al\textsubscript{2}O\textsubscript{3} support and 5% Co catalyst. Unlike previous work, the average plasma power (W) was estimated as the product of the energy dissipated per cycle (the area enclosed by the Lissajous figure) and the cycle frequency. An optical fiber was connected to an Ocean Optics USB 2000+ spectrometer, and emission data were recorded using an integration time of 200 ms and scans to average of 200. The criterion was to maximize the exposure time (integration time) in order to get as much signal as possible before the signal was saturated. This process was not trivial because the packed catalytic material is not completely transparent and scatters light emitted by the DBD.

4.5.1 Findings

Again, the analysis was focus on the second positive system. Figure 4.12 shows the spectrum obtained for the support-only (Al\textsubscript{2}O\textsubscript{3}) and the different supported metal catalysts in the wavelength range 300-385 nm, corresponding to the second positive system of N\textsubscript{2}. Although limited by the resolution of our spectrometer, qualitatively there is no difference between the spectra; a simple analysis looking at the ratio of prominent peaks for each case also confirmed this (Figure 4.13).
Figure 4.12: Optical emission spectra in the L-shaped DBD reactor for different supported metal catalyst and support-only. For all cases, the reactor was run with a power of 15 W, a total flow rate of 40 sccm, a reactant ratio $N_2/H_2=3$, and $L_{pl}/L_{outer} \sim 1/6$.

Figure 4.13: Ratio of prominent peaks for different supported metal catalyst and support-only. For all cases, the reactor was run with a power of 15 W, a total flow rate of 40 sccm, a reactant ratio $N_2/H_2=3$, and $L_{pl}/L_{outer} \sim 1/6$.

By fitting the emission spectra using the commercial software SPECAIR™, $T_{rot}$ and $T_{vib}$ were obtained for each case. Here, there is an important difference from the
previous work, because it was not assumed that $T_{rot} \approx T_{gas}$. The fitting analyses were performed separately over two wavelength ranges: 300-345 nm (Figure 4.14a) and 345-385 nm (Figure 4.14b), and the reported results were obtained by taking the average of $T_{rot}$ and $T_{vib}$ from both bands. The estimated N$_2$ vibrational temperature (Figure 4.14c) had a weak dependence of the type of catalyst bed, remaining around 3100 K on average. At the same time, the rotational temperature (Figure 4.14c) showed similar values for the different supported metal catalysts, and these were slightly greater than $T_{rot}$ for the support-only (Al$_2$O$_3$). These results were consistent with the electrical measurements introduced in Chapter 3 and suggest that there is no appreciable change in plasma thermodynamic properties due to different metal catalysts.

![Example of fitting an experimental spectrum using SPECAIR™ for Co/Al$_2$O$_3$ in the wavelength ranges (a) 305-345 nm and (b) 345-385 nm. (c) Scatter columns for rotational and vibrational temperature values with their respective averages and 95% confidence interval error bars. For all cases, the reactor was run at 15 W, a total flow rate of 40 sccm, a reactant ratio N$_2$/H$_2$=3, and L$_{pib}$/L$_{outer}$~1/6.](image)
4.6 Summary of Findings

Unlike thermal catalysis, our collaborators showed ammonia yield using a packed bed DBD reactor operating close to atmospheric conditions. Additionally, they found the rates of ammonia synthesis over the materials considered (Figure 3.2), including Fe/Al$_2$O$_3$, Ni/Al$_2$O$_3$, and Co/Al$_2$O$_3$, were different (Co > Ni > Fe).

The fundamental mechanisms behind catalytically-enhanced plasma ammonia synthesis are not fully understood. Plasma characterization was focused towards understanding ammonia synthesis enhancement by DBD generated vibrationally-excited N$_2$. Through OES measurements and their respective post-processing data, the estimated N$_2$ vibrational temperature had a weak dependence of the gas composition and the type of catalyst bed, which value was approximately 3000 K. This data was used as input into a microkinetic model to analyze the effect of vibrational excitation on the overall synthesis process and model the interaction of excited states with different catalysts.

Finally, the vibrational temperature as function of metal catalyst was studied. The hypothesis was a higher value of this parameter could imply more N$_2$ dissociation, and therefore this fact could explain differences in the ammonia rates. However, the trend of the vibrational temperature was the opposite of the ammonia rates. Additionally, there is weak dependence of this parameter with respect to the type of catalyst bed.
CHAPTER 5:
HIGH TEMPERATURES

5.1 Introduction

Our collaborators also measured NH$_3$ yields at elevated temperatures in a packed-bed DBD reactor with external heating. NH$_3$ yield curves at different power show a local maximum around 650°C. These results raise questions about which conditions in the system could lead to this type of behavior. The role of excited species in the plasma and their impact at elevated temperatures might be an important factor to consider when studying this phenomenon.
The goals of this research are to explore and analyze the effect of the catalyst/support system on the plasma’s behavior in a packed bed DBD reactor with and without external heating and, to correlate the results with the rate of conversion reactants to products, such as NH₃.

5.2 Experimental Set-Up

The experimental set up for this study was nearly identical to the setup shown in Figure 4.3. A schematic of this experimental set-up is introduced in Figure 5.2. The experiment was carried out in an L-shaped quartz reactor tube consisting of an 8 mm outer diameter with 5 mm inner diameter bent at a 90 degree angle. The reactor consisted of a tungsten rod (used as the inner electrode) centered in a quartz reactor tube wrapped in a stainless-steel mesh (used as the outer electrode). The tube reactor then was wrapped in heating tape. The reactor tube’s length was extended in both legs (horizontal and vertical) in order to have more surface to heat up it. The heating tape was connected to a...
variable voltage regulator transformed, 0-120 V output. To control and measure the temperature, a K thermocouple probe was installed downstream of the frit. The K thermocouple probe was connected to a digital thermometer temperature tester dual point-contact (HH12B). To generate the DBD plasma, a tungsten electrode (1.5 mm diameter) was inserted into the reactor tube and a 6 cm long stainless-steel mesh electrode was attached to the outside. The DBD plasma was driven by an AC power supply (PVM500) using a sinusoidal waveform at ~ 20 kHz; the plasma power was maintained at 15 W for all measurements. Spectra were obtained using an ANDOR Shamrock SR-303i spectrograph with an 1800 lines/mm intensified CCD camera through a fiber optic cable. Exposure times for these measurements were 100 ms and 50 accumulations for 335–413 nm with maximum intensifier gain.
5.3 Results

Unlike chapter 3, all the following were obtained using the L-shaped reactor, which has an outer diameter of 8 mm and an internal diameter of 5 mm. Experiments were performed under the following conditions: 15 W DBD alone, 15 W DBD with 100 mg of Al₂O₃, and 15 W DBD with 100 mg of Fe/Al₂O₃.

First, Lissajous plots were analyzed from two different perspectives: qualitative and quantitative. In general, as Figure 5.3 demonstrates for all analyzed temperatures, in the experiment with Al₂O₃ alone and metal catalyst (Fe) similar parallelogram-like shaped Lissajous can be observed. However, the $C_{\text{plasma-off}}$ increases and applied voltage
decreases with increasing the temperature. Additionally, at high temperatures, the Lissajous plot appears more almond-shaped than like a parallelogram.

Figure 5.3: Lissajous plots for (a) Al$_2$O$_3$-day 1, (b) Al$_2$O$_3$-day 2, (c) Fe/Al$_2$O$_3$-day 1, (d) Fe/Al$_2$O$_3$-day 2. For all these cases, the reactor was run at 15 W, a total flow rate of 40 sccm, a reactant ratio of N$_2$/H$_2$=3, and $L_{pb}/L_{outer}$~1/6.

These variations in the Lissajous plot as a function of temperature can be interpreted as an expansion of the plasma. This fact was verified by inspection during the experiments. Peeters et al [84] introduced the concept of a partial surface discharge to
analyze a DBD reactor. To interpret the Lissajous plot, these authors [84] suggested an equivalent circuit where the reactor is divided into a discharging (β) and non-discharging (α). Both parts are related by the following relation: α + β = 1. The interpretation of the non-discharging has an additional physical meaning, and it can be considered as parasitic capacitance [53].

The discharging part (β) was calculated using the following expression:

\[ β = \frac{C_{\text{plasma-on}} - C_{\text{plasma-off}}}{C_{\text{die}} - C_{\text{plasma-off}}} \]  \hspace{1cm} (5.1)

where \( C_{\text{die}} \) is the dielectric capacitance of the dielectric barrier, which is calculated as 27 pF (37 pF in the case of the straight reactor) based on the cylindrical geometry and dielectric constant of the quartz tube used in this reactor [66]. Here (Equation 5.1), a value of \( β = 1 \) indicates that the discharge consumes the entire surface of the electrode, and \( β = 0 \) indicates that there is no discharge. Figure 5.4 shows that \( β \) increases with increasing the temperature, starting for a \( β \) value slightly greater than 1. Values reported of \( β \) greater than 1 was also found using the data from our collaborators (Professor Hicks group at the University of Notre Dame) operating at 15 W for the reason that the model introduced by Peeters et al [84] fails when the expansion of the plasma is greater than the outer electrode’s length. Additionally, to verify that this trend is not due to a modification in the experimental procedure, the data in Figure 5.4 is presented from two different days, meaning the reactor was loaded with a new packing bed material and rewrapped with heater tape.
Figure 5.4: Discharging factor ($\beta$) as a function of temperature. For all these cases, the reactor was run at 15 W, with a total flow rate of 40 sccm, a reactant ratio of N$_2$/H$_2$=3, and $L_{pb}/L_{outer}$~1/6.

A more detailed analysis of the filamentary behavior using the methods from the previous work [58], shows that the filamentary characteristics change with temperature (Figure 5.5, Figure 5.6, and Figure 5.7), especially beyond 300 °C. Additional results can be found in Appendix E. These parameters seem to be insensitive to temperature variation when operated in a gas temperature below 300 °C. However, above 300 °C, there was not a clear trend of the different filamentary characteristics from all studied configurations (DBD-only, DBD/Al$_2$O$_3$, and DBD/Fe/Al$_2$O$_3$). For instance, the average lifetime of the current increased with the temperature in the case of the DBD-only configuration, but for support-only (DBD/Al$_2$O$_3$) and catalyst-support (DBD/Fe/Al$_2$O$_3$) configurations, the trend was reversed. More interesting was that at higher temperatures (above ~300 °C) the lifetime filamentary current starts to decrease in both scenarios, following the same trend as DBD-only. A similar analysis was performed for the number
of filaments, in which all the configurations above ~300 °C follow the same trend, meaning the number of filaments decayed as the gas temperatures increased.

Figure 5.5: Plots of data extracted from current traces for DBD experiments at 15 W with a gas composition of N₂/H₂=3, a total flow rate of 40 SCCM for five different temperatures: (a) the time-averaged filamentary current per half cycle, (b) average number of filaments per half cycle, (c) average current per filament, (d) average lifetime per filament.
Figure 5.6: Plots of data extracted from current traces for DBD/γ-Al₂O₃ background experiments at 15 W with a gas composition of N₂/H₂=3, a total flow rate of 40 SCCM for five different temperatures: (a) the time-averaged filamentary current per half cycle, (b) average number of filaments per half cycle, (c) average current per filament, (d) average lifetime per filament.
Figure 5.7: Plots of data extracted from current traces for DBD/Fe/γ-Al2O3 background experiments at 15 W with a gas composition of N₂/H₂=3, a total flow rate of 40 SCCM for five different temperatures: (a) the time-averaged filamentary current per half cycle, (b) average number of filaments per half cycle, (c) average current per filament, (d) average lifetime per filament.

Finally, OES measurements were performed under the following conditions: 15 W DBD-only, 15 W DBD with 100 mg of Al₂O₃, and 15 W DBD with 100 mg of Fe/Al₂O₃. Figure 5.8, 5.9, and 5.10 show the emission spectra for these configurations.

The introduction of a catalyst into the reactor made the spectra noisier as shown in Figure
5.10. Qualitatively there is no difference between the spectra; a simple analysis looking at the ratio of prominent peaks for each case confirmed this.

Figure 5.8: Emission spectra of a 15 W DBD for different temperatures. Measured spectra centered at (a) 338 nm and (b) 356 nm.

Figure 5.9: Emission spectra of a 15 W DBD/Al₂O₃ for different temperatures. Measured spectra centered at (a) 338 nm and (b) 356 nm.
Figure 5.10: Emission spectra of a 15 W DBD/Ni/Al$_2$O$_3$ for different temperatures. Measured spectra centered at (a) 338 nm and (b) 356 nm.

Just as in Chapter 4, the N$_2$ vibrational and rotational temperatures were extracted by comparing spectroscopy measurements with a modeled optical emission using the Software SPECAIR™ (Figure 5.11). The vibrational temperature (Figure 5.12) was obtained in the wavelength range of 350-363 nm (Figure 5.11) using the data shown in (Figure 5.8-b) from DBD-only, and these results were compared to the wavelength range 368-382 nm (Error! Reference source not found.). Figure 5.12 shows that the N$_2$ vibrational temperature has a clear trend that is dependent on the temperature, decaying almost linearly as the gas temperature increases. However, this functional relation is relatively weak.
Figure 5.11: N₂ peaks was in the spectrum centered at (a) 354 nm and (b) 374 nm (red dots). All these peaks belong to the second positive electronic transition. The fitting process was performed using SpecAir™.

Figure 5.12: N₂ vibrational and rotational temperature as a function of the gas temperature. For this analysis, the gas temperature range was between 150 °C and 576 °C.

5.4 Summary of Findings and Conclusions

The techniques explored in Chapter 3 and Chapter 4 were used in this Chapter. Increasing the gas temperature induced an expansion of the plasma that was verified by
inspection and using the partial discharging model for DBD introduced by Peters et al. [84]. The influence of the temperature on the filamentary characteristics was analyzed in the range of ~120-500 °C. Below ~300 °C, these filamentary characteristics showed temperature insensitivity. However, at higher temperatures (above 300 °C), these filamentary characteristics showed a clear trend no matter the configuration (DBD-only, DBD/Al$_2$O$_3$, DBD/Fe/Al$_2$O$_3$). More specifically, the number of filaments decreased, and the lifetime of the filaments increased as the gas temperature increased. The non-equilibrium nature of the plasma creates a reactive medium in which different excited-species live. This characteristic could explain the production of ammonia close to atmospheric conditions. Based on the last argument, the superposition of effects, a greater lifetime of the filaments and the approach to the pseudo-thermal equilibrium would be of no benefit to the reaction process (ammonia production) at higher temperatures. However, it is necessary to perform experiments at higher temperatures (~650 °C) in order to have a clear picture of the trend of the number and lifetime of the filaments. From the OES measurements it was found that the vibrational temperatures (~3000 K) decreased linearly with respect to the gas temperature. However, this functional dependence was weak.
CHAPTER 6:
GENERAL CONCLUSIONS AND FUTURE WORK

6.1 General Conclusions

A comprehensive study of the interaction between plasma and catalyst is crucial to better understanding the synergetic effects of kinetic performance for a chemical reaction. In a simplistic way, the interactions between the two can be separated into two categories: the effects of plasma on the catalyst and the effects of the catalyst on the plasma. The work presented here focuses on the latter, with the aim of filling a void in this part of the literature.

To conduct these measurements, a DBD plasma reactor was built. This reactor was identical to the one used in the plasma-assisted catalysis measurements, save for a small modification allowing better optical access. Multiple experimental techniques were employed to characterize the system under different packed bed conditions, including optical emission spectroscopy (OES), current-voltage (I-V) measurements, and charge-voltage (Q-V) measurements. Data from these macroscopic measurements of DBD properties were then compared with the results of the ammonia yield and ammonia rate. Hypothesizing that a change in kinetic performance would correspond to changes in macroscopic properties, patterns between the two data sets were explored. Additionally, the role of excited species (specifically vibrational) in ammonia synthesis was studied.
From the results of our collaborators, the catalytic measurements of N\textsubscript{2} fixation with and without oxide-supported metal catalysts showed that the production of ammonia depends on the nitrogen-hydrogen (N\textsubscript{2}/H\textsubscript{2}) ratio. OES measurements of atmospheric pressure DBD plasmas were performed under the same operational conditions with different N\textsubscript{2}/H\textsubscript{2} ratios. Using the techniques listed above, the macroscopic DBD properties were measured as a function of different catalyst materials. This data showed no statistically significant trends (using ANOVA+ Tukey analysis) between all analyzed metal-on-oxide support configurations (regardless of metal) for any macroscopic DBD properties. Using OES, it was determined that the estimated N\textsubscript{2} vibrational temperature had a weak dependence on the gas composition and had approximate values of 2800-3000 K.

A new reactor was designed in order to determine if the catalyst or support modifies the plasma at elevated temperatures. Macroscopic DBD properties were again compared with the corresponding rate and yield measurements by our collaborators running a similar reactor under the same conditions. At elevated temperatures there was practically no modification of the plasma’s macroscopic properties.

The lack of correlations suggest that the catalyst and support had no appreciable impact on the macroscopic plasma properties even for experimental conditions and configurations with different reaction kinetics. Ultimately, this work shows that any synergy that occurs during ammonia synthesis in this plasma-catalyst system is not due to any catalyst modification of plasma that can be resolved on the macroscale.
6.2 Future Work

Analyze the production of NH\textsubscript{x} under different plasma conditions including the influence of the catalytic materials on DBD reactors using a high-resolution OES.

Key Question(s):

a) Does the catalyst/support modify the production of NH\textsubscript{x} species?

b) Does this modification in the production of NH\textsubscript{x} species play an important role in the production of NH\textsubscript{3}?

One critical species detected by other researchers is NH\textsubscript{c}, which was previously not detected in my prior work. The presence of this intermediate species raises a question about the chemical pathways from reactants to products and the plasma-catalyst’s role in said reactions. Does the plasma-catalyst interaction promote the hydrogenation of adsorbed NH species in addition to/rather than dissociating excited N\textsubscript{2}, since the plasma can (at least partially) achieve this dissociation on its own? Gas phase NH\textsubscript{x} species would then be desirable to measure since they are proposed to play a significant role in NH\textsubscript{3} production. For instance, Uyama [85] et. al reported that the NH radical is the principal precursor for production of NH\textsubscript{3} in the gas phase. They suggested that the mechanism to form NH is given by:

\begin{align*}
N_2 + e^- &\rightarrow N_2^+ + 2e^- \\
H_2 + e &\rightarrow H_2^+ + 2e^- \\
N_2^+ + H_2 &\rightarrow N_2H^+ + H \\
N_2^+ + H &\rightarrow N_2H^+ \\
N_2H^+ + e^- &\rightarrow NH + N
\end{align*}
$N + H \rightarrow NH$ \hspace{1cm} (5.6)

To resolve NH$^*$ lines, a spectrometer with higher resolution than the Ocean Optics USB 2000+ spectrometer is required. Ocean Optics 2000+ spectrometer has an optical resolution of 1.5 nm. For instance, the Ocean Optics USB 2000+ spectrometer cannot distinguish the NH emission line at 336 nm [85] from the emission line at 337 nm. However, the Andor Shamrock 303i imaging spectrometer has an optical resolution of 0.43 nm, 0.1 nm, and 0.06 nm [73], which should be sufficient to resolve these NH$^*$ lines [72]. Also, because of its higher resolution, the Andor Shamrock 303i should provide more accurate estimates of the electron, vibrational, and electronic temperatures.

Based on the work of Muller et al. [86], the NH emission lines at 324.3 nm, 336.3 nm, 337.4 nm, and 338.9 nm could be identified. These results could be contrasted against the emission lines for N$_2^+$ (391.1 nm) and potentially N (746.2) for different concentrations of the reactants (N$_2$/H$_2$) to shed light on the production of NH$_x$. This data could then be correlated to conversion measurements of N$_2$ to NH$_3$.  

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APPENDIX A:

KINETIC MEASUREMENTS

A.1 Characterization of Ammonia Synthesis Rates.

Ammonia (NH₃) synthesis rates for the support-only and different metal-support combinations were characterized by varying the total flow rate from 25 to 55 mL min⁻¹ and measuring the amount of NH₃ produced. Figure A.1 shows the measured NH₃ produced as a function of the residence time (W/F) of the reactant in the reactor for each catalyst at a constant temperature of 200°C and discharge power of 15 W. The background reaction was also measured by doing the experiment with the Al₂O₃ support only.
Figure A. 1 Observed rates as a function of the residence time of reactants (W/F) in the DBD reactor. Reaction conditions: N\textsubscript{2} : H\textsubscript{2} = 3:1, total pressure = 1 atm, plasma power = 15 W, reactor temperature = 473 K. Error bars indicate the standard deviation in the rates.
APPENDIX B:

ANOVA (ANALYSIS OF VARIANCE) WITH POST-HOC TUKEY HSD
(HONESTLY SIGNIFICANT DIFFERENCE)

Analysis of variance (ANOVA) [87] is a statistical method which is generally used for comparing two or more means by analyzing variance. ANOVA tests general differences among the means of the populations. The null hypothesis ($H_0$) states that all the means ($\mu_1$, $\mu_2$, ..., $\mu_k$) are equal, if it is rejected it can be concluded that there is at least one statistical difference between the means.

$$H_0: \mu_1 = \mu_2 = \cdots = \mu_k$$

The ANOVA is not suitable for determining which population means are different from each other. For more specific analysis the Tukey "Honestly Significantly Different" (HSD) test can be used. Depending on how many independent variables so called factors are in the experiment one-way, two-way or k-way ANOVA can be applied. This study assumes equal sample size and uses one-way ANOVA; therefore, the process is introduced according to that. There are three important assumptions must be considered to use ANOVA:

- Normal distribution
- Same variance for each population
- Independently sampled values
The ANOVA uses two different ways to estimate the population variance ($\sigma^2$): variance within groups – mean square error (MSE) and variance between groups – mean square between (MSB).

MSE always estimates $\sigma^2$ even if the population means are not the same ($H_0$ is rejected) and it can be calculated as the mean of the group variances. On the other hand, MSB estimates $\sigma^2$ assuming that the population means are the same. If the $H_0$ is rejected (population means are not equal) MSB estimates larger quantity than $\sigma^2$. The calculation of the MSB is based on the sampling distribution of the mean ($\sigma_M^2$), which is shown in Equation B.1, where $n$ is the sample size of each group.

$$\sigma_M^2 = \frac{\sigma^2}{n}$$  \hspace{1cm} (B.1)

The sampling distribution of the mean can be estimated with the variance of the group means and then multiplying it by $n$ we can get the $\sigma^2$. Testing the null hypothesis MSE and MSB must be compared. If MSB is much larger than MSE, then the population means are not likely to be the same. In order to determine whether the difference is big enough the F ratio has to be calculated as the ratio of MSB and MSE and the sample size has to be considered (small samples are more unstable, and it can have higher F ratio).

Based on the sampling distribution of F the probability value can be determined (the area of the right of the F-ratio value in the distribution curve – black area in Figure B. 1) and the null hypothesis can be rejected or not. The F distribution curve’s shape can vary based on the degrees of freedom parameters (df) for the numerator (MSB)= $k-1$ and the denominator (MSE)= $N-k$, where $k$ is the number of groups and $N$ is the total number of observations.
The Tukey HSD test can determine the pairs where the difference occurred in the means. This method is using the following formula for each pair, where $M_i - M_j$ is the difference between the pair of means and $n$ is the sample size of each group.

\[ Q = \frac{M_i - M_j}{\sqrt{\frac{MSE}{n}}} \]  \hspace{1cm} (B.2)

The probability value for $Q$ can be determined with the studentized range calculator. The degrees of freedom are the same than for MSE.
APPENDIX C:
LISSAJOUS CODE

The following corresponds to the MATLAB™ routine used for estimating the power and the capacitances of the system ($C_{\text{plasma-on}}$ and $C_{\text{plasma-off}}$).
FileName = files{fileNameIndex};
filePath = fullfile(PathName,FileName);

disp(' ')
disp(['File: ', FileName])

data= csvread(filePath,...
    0, 0,[0 0 100000 2]);

time=data(:,1);
voltage=data(:,2);
charge=data(:,3);

L=length(voltage);
time=linspace(time(1),time(L),L);
time=time';

    % Convert Channels
    V = voltage; % CH1 is overall system voltage (attenuated by 1000x)
    Q = charge; % CH2 is the voltage across the resistor
    TIME=time;

    F = fit(TIME, V, 'sin1');
    freq=F.b1/(2*pi);

    % Calculate timestep
    dt = TIME(2) - TIME(1);

    % Calculate Period
    period = 1/freq;

    V1_index = round(0.5*(length(TIME) - period/dt));
    V2_index = round(0.5*(length(TIME) + period/dt));

    % Calculate polygon area
    area = polyarea(V(V1_index:V2_index), Q(V1_index:V2_index));
    Vs=V(V1_index:V2_index);
    Qs=Q(V1_index:V2_index);

    % Calculate alternative power based on peak to peak distance (freq)
    P2 = freq*area;

    % Display results
    disp(['Power: ', num2str(P2), ' W'])
    disp(['Frequency: ', num2str(freq), ' Hz'])
    hold on
    % end

File: Power3.csv
C.3 average

\[
\begin{align*}
V_a &= \text{zeros}(V_2\_index-V_1\_index,1); \\
Q_a &= \text{zeros}(V_2\_index-V_1\_index,1); \\
k &= \text{floor}(\text{TIME}(\text{end})/\text{period}) - 1; \\
V_1\_index &= 1:\text{round}(\text{period}/dt) : \text{length}(\text{TIME}); \\
\text{Areas} &= \text{arrayfun}(@(s,e) \text{polyarea}(V(s:e), Q(s:e)), V_1\_index(1:end-1), V_1\_index(2:end)-1); \\
\text{Powers} &= \text{Areas} / \text{period}; \\
\text{Power\_average} &= \text{sum}(\text{Areas}) / (\text{TIME}(V_1\_index(\text{end})) - \text{TIME}(V_1\_index(1))) \\
\text{Area\_average} &= \text{mean}(\text{Areas}) \\
\text{minV} &= \text{min}(V); \\
\text{maxV} &= \text{max}(V); \\
\text{minQ} &= \text{min}(Q); \\
\text{maxQ} &= \text{max}(Q); \\
\text{C\_stray} &= (\text{maxQ} - \text{minQ}) / (\text{maxV} - \text{minV}); \\
a1 &= \text{find}(((V - \text{minV}) == 0) \& ((Q - \text{minQ}) == 0)); \\
a2 &= \text{find}(((V - \text{maxV}) == 0) \& ((Q - \text{maxQ}) == 0)); \\
\text{if}  (\text{isempty}(a2) == 1) \\
\quad a2 &= \text{find}((V - \text{maxV}) == 0); \\
\text{end} \\
\text{if}  (\text{isempty}(a1) == 1) \\
\quad a1 &= \text{find}((V - \text{minV}) == 0); \\
\text{end} \\
y0 &= Q(a1(1)); \\
y1 &= Q(a2(1)); \\
x0 &= V(a1(1)); \\
x1 &= V(a2(1)); \\
k1 &= \text{find}(Q > y0 + (V-x0) \cdot (y1-y0)/(x1-x0)); \\
k2 &= \text{find}(Q < y0 + (V-x0) \cdot (y1-y0)/(x1-x0));
\end{align*}
\]
data = sortrows([V(k1), Q(k1)]); data2 = sortrows([V(k2), Q(k2)]);
[r,m,b] = regression(data(:,1),data(:,2),'one');

% left data
[index1,index2]=size(data);
% right data
[index11,index22]=size(data2);

for i=2:100:index1
    [r,m,b] = regression(data(1:i,1),data(1:i,2),'one');
    mdl1=LinearModel.fit(data(1:i,1),data(1:i,2));
    error1=mdl1.Coefficients.SE;
    ii1(i-1)=i-1;
    rr1(i-1)=r;
    mm1(i-1)=m;
    bb1(i-1)=b;
    err1(i-1)=error1(2);
end

for i=2:100:index11
    [r,m,b] = regression(data2(1:i,1),data2(1:i,2),'one');
    mdl2=LinearModel.fit(data2(1:i,1),data2(1:i,2));
    error2=mdl2.Coefficients.SE;
    ii2(i-1)=i-1;
    rr2(i-1)=r;
    mm2(i-1)=m;
    bb2(i-1)=b;
    err2(i-1)=error2(2);
end

j=0;
for i=1:100:index1-1
    [r,m,b] = regression(data(index1-i:index1,1),data(index1-i:index1,2),'one');
    mdl3=LinearModel.fit(data(index1-i:index1,1),data(index1-i:index1,2));
    error3=mdl3.Coefficients.SE;
    ii3(i)=i+1;
    rr3(i)=r;
    mm3(i)=m;
    bb3(i)=b;
    err3(i)=error3(2);
end

for i=1:100:index11-1
    [r,m,b] = regression(data2(index11-i:index11,1),data2(index11-i:index11,2),'one');
    mdl4=LinearModel.fit(data2(index11-i:index11,1),data2(index11-i:index11,2));
    error4=mdl4.Coefficients.SE;
    ii4(i)=i+1;
    rr4(i)=r;
mm4(i)=m;
bb4(i)=b;
err4(i)=error4(2);
end

minim=5000;
maxim=40000;

rrr1=rr1(minim:size(rr1,2));
rrr2=rr2(minim:maxim);
rrr3=rr3(minim:maxim);
rrr4=rr4(minim:size(rr4,2));

mmm1=mm1(minim:size(rr1,2));
mmm2=mm2(minim:maxim);
mmm3=mm3(minim:maxim);
mmm4=mm4(minim:size(rr4,2));

err11=err1(minim:size(rr1,2));
err22=err2(minim:maxim);
err33=err3(minim:maxim);
err44=err4(minim:size(rr4,2));

final1=find(max(rrr1)-rrr1==0);
final2=find(max(rrr2)-rrr2==0);
final3=find(max(rrr3)-rrr3==0);
final4=find(max(rrr4)-rrr4==0);

C.4 Output Data to datamfinal

if ~exist('datamfinal', 'var') %it doesn't exist, create new
labels={'File Name',... 'C_{plasma-on} left branch, (pF)',...
'C_{plasma-off} left branch, (pF)',...
'C_{plasma-on} right branch, (pF)',...
'C_{plasma-off} right branch, (pF)',...
'power average, (W)',...
'C_stray (pF)','error1','error2','error3','error4'};

values={FileName, mmm1(final1)*1e12,mmm2(final2)*1e12,...
mmm4(final4)*1e12,mmm3(final3)*1e12,Power_average,C_stray,err11(final1)*1e12,err22
(final2)*1e12,err33(final3)*1e12,err44(final4)*1e12};
datamfinal=vertcat(labels, values);
else %if it exists concatenate onto existing datamfinal
datamfinal=vertcat(datamfinal, {FileName, mmm1(final1)*1e12,...
    mmm2(final2)*1e12,...
    mmm4(final4)*1e12, mmm3(final3)*1e12, Power_average, C_stray, err11(final1)*1e12, err22
    (final2)*1e12, err33(final3)*1e12, err44(final4)*1e12});
end

% %adjust Lissajous figure to the center of XY axis.
set(gcf, 'Units', 'Inches', 'Position', [0, 0, 3.25, 2.75],...
    'PaperUnits', 'Inches', 'PaperSize', [3.25, 2.75])
shift=(max(charge)+min(charge))./2.*1e9;
plot(voltage*1e-3,charge*1e9-shift,'o','MarkerSize',2)
title('15W DBD/Al\textsubscript{2}O\textsubscript{3}')
xlabel('voltage, (kV)')
ylabel('charge, (pF)')
ylim([-100 100])
legend('135 C','152 C','195 C','248 C','311 C','371 C','457 C')
set(gca, 'FontSize',11)
hold on

Warning: Ignoring extra legend entries.

15W DBD/Al\textsubscript{2}O\textsubscript{3}

charge, (pF)

voltage, (kV)

end

%Sets variable "dfilePath" to put visible filepath closer to datamfinal.m
    dfilePath=filePath((length(filePath)*0.5-7):end);
figure
subplot(1,2,1)
plot(ii1,mm1*1e12, ii4, mm4*1e12, 'Linewidth',1)
title('Data from last file')
xlabel('number of data, (a.u.)')
ylabel('C_{plasma-on}, (pF)')
% ylim([3 8])
 subplot(1,2,2)
 plot(ii1,rr1,ii4,rr4,'LineWidth',1)
 xlabel('number of data, (a.u.)')
 ylabel('correlation factor, (a.u.)')
 ylim([0.95 1.05])

 figure
 subplot(1,2,1)
 title('Data from last file')
 plot(ii2,mm2*1e12,ii3,mm3*1e12,'LineWidth',1)
 ylim([3 8])
 title('Data from last file')
 xlabel('number of data, (a.u.)')
 ylabel('C_{plasma-off}, (pF)')
 subplot(1,2,2)
 plot(ii2,rr2,ii3,rr3,'LineWidth',1)
 xlabel('number of data, (a.u.)')
 ylabel('correlation factor, (a.u.)')
 ylim([0.95 1.05])

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APPENDIX D:

ELECTRICAL CHARACTERIZATION

D.1 Configuration Oscilloscope for 2.5 W and 15 W.

**Oscilloscope:** four-channel high definition oscilloscope (LeCroy HDO4054A).

**Sampling rate:** 2.5 GS/s (equivalent to 0.4 ns).

**Channel 1 (voltage):** 2 kV/div (screen limits=±8 kV).

**Channel 2 (current):** 1 A/div (screen limits=±4 A).

**Timebase:** 20 μs/div (screen limits=200 μs).
D.2 Electrical Characterization for $L_{pb}/L_{outer} \sim 1/6$

The macroscopic electrical properties studied for $L_{pb}/L_{outer} \sim 1/6$ show similar behavior for all studied flow rates, as shown in the Figure D. 2 - D. 9. These values were obtained from 12-bit data with a time window of 200 µs, which means four negative and positive half-cycles. Figure D. 2 – D. 5 were obtained under the following conditions: 15 W, total flow rate of 30 sccm, a reactant ratio $N_2/H_2=3$, and $L_{pb}/L_{outer} \sim 1/6$. 

Figure D. 1 Screen shot from LeCroy HDO4054A oscilloscope with the configuration used during the experiments.
Figure D. 2 Extracted time-average filamentary current per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for time-average peak current values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

Figure D. 3 Extracted average number of filaments per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for average number of filaments values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.
Figure D. 4 Extracted average current of the filaments per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for average current of the filaments values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

Figure D. 5 Extracted average lifetime of each filament per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for average lifetime of each filament values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.
Figure D. 6 – D. 9 were obtained under the following conditions: 15 W, a total flow rate of 50 sccm, a reactant ratio $\text{N}_2/\text{H}_2=3$, and $L_{\text{pb}}/L_{\text{outer}} \sim 1/6$.

Figure D. 6 Extracted time-average filamentary current per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for time-average filamentary current values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.
Figure D. 7 Extracted average number of filaments per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for average number of filaments values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

Figure D. 8 Extracted average current of the filaments per half-cycle shows little variation between the different metal catalysts. Panel (a) shows scatter columns for average current of the filaments values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.
Figure D. 9 Extracted average lifetime of each filament per half-cycle shows little variation between the different metal catalysts.

Panel (a) shows scatter columns for average lifetime of each filament values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

D.3 Summary of Site-Time Yield as Function of the Electrical Metrics for $L_{pb}/L_{outer} \sim 1/6$.

The site-time yield as a function of filament properties are shown in Figure D. 10.

For all cases, the reactor was run at 15 W, a total flow rate of 40 sccm, a reactant ratio $N_2/H_2=3$, and $L_{pb}/L_{outer} \sim 1/6$.  

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Figure D. 10 Measured ammonia STYs as function of (a) the time-average filamentary current, (b) average number of filaments, (c) average filament current, and (d) average filament lifetime. For the electrical characterization, the reactor was run at 15 W, a total flow rate of 40 sccm, a reactant ratio N₂/H₂ = 3, and \( L_{pb}/L_{outer} \sim 1/6 \).

D.4 Electrical Characterization for \( L_{pb}/L_{outer} \sim 1 \)

The macroscopic electrical properties studied for \( L_{pb}/L_{outer} \sim 1 \) are shown in the Figures D. 11 -D. 14. The conditions for all these measurements were at 2.5 W, a total flow rate of 40 sccm, and reactant ratio of N₂/H₂ = 3. These values were obtained from 12-bit data with a time window of 200 μs, which means four negative and positive half-
cycles.

Figure D. 11 Extracted time-average filamentary current per half-cycle. Panel (a) shows scatter columns for time-average peak current values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

Figure D. 12 Extracted average number of filaments per half-cycle. Panel (a) shows scatter columns for average number of filaments values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.
Figure D. 13 Extracted average current of the filaments per half-cycle. Panel (a) shows scatter columns for average current of the filament values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.

Figure D. 14 Extracted average lifetime of each filament per half-cycle. Panel (a) shows scatter columns for average lifetime of each filament values with their respective averages and 95% confidence interval error bars. Panel (b) shows the ANOVA + Tukey analysis comparing mean values.
APPENDIX E:

ELECTRICAL CHARACTERIZATION AT HIGH TEMPERATURES
E.1 Electrical Characterization at High Temperatures for Different Configurations (DBD-only, DBD/Al₂O₃, and DBD/Fe/Al₂O₃).

Figure E. 1: Plots of data extracted from current traces for DBD experiments at 15 W with a gas composition of N₂/H₂=3, a total flow rate of 40 SCCM for five different temperatures: (a) the time-averaged filamentary current per half cycle, (b) average number of filaments per half cycle, (c) average current per filament, (d) average lifetime per filament.
Figure E.2: Plots of data extracted from current traces for DBD/Al₂O₃ experiments at 15 W with a gas composition of N₂/H₂=3, a total flow rate of 40 SCCM for five different temperatures: (a) the time-averaged filamentary current per half cycle, (b) average number of filaments per half cycle, (c) average current per filament, (d) average lifetime per filament.
Figure E. 3: Plots of data extracted from current traces for DBD/Fe/Al2O3 experiments at 15 W with a gas composition of N2/H2=3, a total flow rate of 40 SCCM for five different temperatures: (a) the time-averaged filamentary current per half cycle, (b) average number of filaments per half cycle, (c) average current per filament, (d) average lifetime per filament.
APPENDIX F:

OPTICAL EMISSION SPECTROSCOPY AT HIGH TEMPERATURES

F.1 Spectra for Different Configurations (DBD-only, DBD/Al₂O₃, and DBD/Fe/Al₂O₃)

Figure F. 1: Emission spectra of a 15 W DBD for different temperatures. Measured spectra centered at (a) 338 nm and (b) 356 nm.
Figure F. 2: Emission spectra of a 15 W DBD for different temperatures. Measured spectra centered at (a) 375 nm and (b) 400 nm.

Figure F. 3: Emission spectra of a 15 W DBD/Al₂O₃ for different temperatures. Measured spectra centered at (a) 338 nm and (b) 356 nm.
Figure F. 4: Emission spectra of a 15 W DBD/Al$_2$O$_3$ for different temperatures. Measured spectra centered at (a) 375 nm and (b) 400 nm.

Figure F. 5: Emission spectra of a 15 W DBD/Al$_2$O$_3$ for different temperatures. Measured spectra centered at (a) 338 nm and (b) 356 nm.
Figure F. 6: Emission spectra of a 15 W DBD/Al\textsubscript{2}O\textsubscript{3} for different temperatures. Measured spectra centered at (a) 375 nm and (b) 400 nm.

Figure F. 7: Emission spectra of a 15 W DBD/Fe/Al\textsubscript{2}O\textsubscript{3} for different temperatures. Measured spectra centered at (a) 338 nm and (b) 356 nm.
Figure F. 8: Emission spectra of a 15 W DBD/Fe/Al$_2$O$_3$ for different temperatures. Measured spectra centered at (a) 375 nm and (b) 400 nm.

F.2 N$_2$ Vibrational and Rotational Temperatures as a Function of the Gas Temperatures.

Figure F. 9: N$_2$ vibrational and rotational temperatures obtained at different wavelength: (a) 350-363 nm, (b) 368-382 nm.
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