AN ABSTRACT OF THE THESIS OF

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Title:Investigation of the Effect of Pulsed Direct Current on Methane Conversion and
Reforming in a Point-to-Point Plasma Discharge Microreactor

Abstract approved:

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Stranded natural gas and biogas comprise a vast energy resource that is mostly wasted via flaring. This represents an opportunity to investigate novel ways to harness this resource. Nonthermal plasmas consist of excited electrons, ions and neutral atoms/molecules that have the ability to disrupt chemical bonds at ambient temperatures and pressures. Methane conversion to value-added products is difficult in industry due to the stability of the C-H bond. The smaller scale of microscale technology offers many benefits including intensified momentum, heat and mass transport using reduced timescales and smaller spaces. Electrode spacing of less than 1 millimeter allows for lower plasma operating voltages (less than 1 kV). Direct current has historically been the type of electricity used to operate the plasma discharge using this particular electrode geometry and spacing. Any potential effects of using other types of electricity such as alternating current and pulsed direct current have not been explored. This work explores the effect of pulsing the current on the conversion, selectivity, yield and specific energy intensity of ethylene and synthesis gas production.

Frequencies of 0 Hz (straight DC), 60 Hz, 500 Hz, 1 kHz, 5 kHz, 10 kHz, 50 kHz and 250 kHz were chosen for this work. Operating parameters were fixed at 15.2 psia pressure, 20-25°C temperature (ambient), 40 sccm flow rate and a 3:1 CO₂:CH₄ molar feed ratio. Three replicates of each run were taken to enable statistical analysis. Chemical analysis was performed using gas chromatography and electrical analysis was performed using an oscilloscope.

Reactor performance was assessed at various frequencies at a duty ratio of 0.5 while keeping the average power at 3.1 W. Conversion was found to be constant when using a constant average power with all runs having around 19-20% average. The lowest and highest experimental values for selectivity ranged from 20.6% \pm 4.04% at 500 Hz to 41.8% \pm 9.63% at 250 kHz. The results of direct current and the results of the highest frequencies examined were not statistically discernable. Lower frequencies involved spurts of higher instantaneous current and power that averaged out to 3.1 W over time. Higher power density equates to a higher incidence of electron impact events at the molecular level. Higher-order hydrocarbons formed at these power levels will have a tendency to undergo more impact events and leave the reactor as lower-energy synthesis gas products.

The specific energy intensity of synthesis gas and ethylene formation was investigated. The lowest and highest experimental values for the specific energy intensity of synthesis gas ranged from 790. \pm 56.0 kJ mol⁻¹ at 10 kHz to 1,120 \pm 105 kJ mol⁻¹ at 250 kHz. Similarly, the lowest and highest experimental values for the specific energy intensity of ethylene ranged from 19,660 \pm 4800. kJ mol⁻¹ at 10 kHz to about 34,900 \pm 9,990 kJ mol⁻¹ at 500 Hz. Lower frequency experimental data showed a higher incidence of synthesis gas production. These specific energy intensities were higher than values from different types of plasma work in literature. The focus of this work was to determine any discernable effects of using pulsed current with the same overall power input. Pulsing direct current promotes the formation of synthesis gas and is detrimental to selectivity towards higher order hydrocarbons. ©Copyright by Adam Shareghi September 14, 2018 All Rights Reserved

Investigation of the Effect of Pulsed Direct Current on Methane Conversion and Reforming in a Point-to-Point Plasma Discharge Microreactor

By Adam Shareghi

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Adam Shareghi, Author

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Thank you to all my friends, family and colleagues that have made my journey possible thus far.

There are way too many of you to name individually.

You know who you are.

I love you all.

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Chapter 1- Introduction

1.1 Stranded Natural Gas Opportunity

Stranded methane sources comprise a significant source of gaseous chemical potential energy. These may be petroleum-based resources of fossil origin or stranded biogas from landfills and farms. The vast majority of this resource is flared on site in absence of the cost-prohibitive pipeline infrastructure that would be required to bring these gases to market for conventional processing [1]. All this energy is essentially wasted from an engineering standpoint since no portion of this heat is being used for any thermal industrial application or extraction of useful work. It is estimated that amounts equivalent to up to 25% of US annual natural gas consumption and 30% of EU annual natural gas consumption are flared (based on 2015 consumption levels). [2] Stranded gas comprises an estimated 60% of proven fossil fuel global gas reserves [3]. Alternative gas utilization has been extensively researched with possible options being: compressed natural gas (CNG), gas to liquids (GTL), gas to chemicals (GTC), gas to solids (GTS) and gas to wire (GTW) [4].

1.2 Fossil Fuel Resource Consumption and Availability

Atmospheric concentrations of carbon dioxide have continued to rise as the industrialized world burns through its reserves of non-renewable fossil fuel resources year after year. Emission rates continue to increase proportionally along with the population and associated economic growth. This has resulted in an observable global warming trend that has become a widely-accepted fact in the scientific community over the past several decades as the available data has become more clear and convincing with advancing

technology [5]. A consequence of increasing global population and economic activity is increased demand for affordable, abundant energy sources. The global economy continues to grow at an average rate of about 3.4% per year. As a result, global energy demand is forecasted to rise about 40% between 2017 and 2040 [6]. Figures 1 and 2 show the supply and demand scenarios of U.S. natural gas supply and demand according to the U.S. Energy Information Administration.



Figure 1: U.S. Natural Gas Supply Outlook through 2050 as of 2017. Note the decreasing conventional resources and increasing reliance on unconventional shale gas supplies (which tend to be more stranded) [7].



Figure 2: U.S. Natural Gas Demand Outlook through 2050 as of 2017. Note the overall steady increase in resource demand primarily in the industrial and electric power sectors [7].

The scenario depicted in Figures 1 & 2 demonstrates the need for researchers to explore potential renewable resources and creative ways to make use of stranded nonrenewable resources that would otherwise be wasted.

1.3 Biogas Opportunity

Biogas consists of primarily CH₄ and CO₂ generated from activity of anaerobic microorganisms. Significant quantities are generated in the waste disposal and agriculture industries. Similarly to stranded fossil gases, these are largely flared or vented to the atmosphere and comprise a substantial portion of worldwide anthropogenic greenhouse gas emissions. Figure 3 shows a graphical breakdown of U.S. emissions of methane by source for the year 2015.

2015 U.S. Methane Emissions, By Source



U.S. Environmental Protection Agency (2017). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2015.

Figure 3: U.S. Methane Emissions by source for the year 2015 [8].

Approximately 53% of total methane emissions are directly a result of biological activity. This amount eclipses the 31% estimated from petroleum and natural gas sources.

Landfill gas (LFG) represents a significant untapped source of combustible gases in addition to stranded natural gas. Approximately 50% of LFG is CH₄ with the balance being primarily CO₂ (with trace amounts of other gases). Municipal solid waste is responsible for 14% of global CH₄ emissions. These emissions are estimated to grow by 9% between 2005 and 2020[9]. By simulating typical biogas mixtures of CH₄ and CO₂, a better understanding can be developed of how various types of nonthermal plasma could be used to convert this stream into one consisting of value added chemicals such as ethylene, higher-order hydrocarbons, etc. This work does not include any analysis regarding treatment of trace species (i.e. hydrogen sulfide, etc.) that would complicate the overall process in a real-world setting.

1.4 How Nonthermal Plasma Utilizes These Opportunities

As implied previously, the gaseous nature of stranded methane sources makes economical transport to market cost-prohibitive in a vast majority of cases. Nonthermal plasma consists of high concentrations of high-energy electrons which bombard the chemical species in the gas phase and disrupt their covalent bonds. Disruption of these bonds enables conversion of the methane into value-added products such as ethylene and higher-order hydrocarbons. If liquid fuels can be produced (C5+), this allows for a much more efficient transport from remote sources. Given that burning fuels is currently the primary way to generate electricity, it would be wasteful to source the electrical input from the grid. This demonstrates the necessity to source the electricity from renewables such as solar power such that any chemical energy derived from this process would essentially be capturing a portion of "renewable" energy. Figure 4 shows an idealized graphical sequence of how a nonthermal plasma could potentially utilize stranded biological or mineral gas resources.





Microscale process technology is defined as process devices that operate on the submillimeter scale (less than 1000 microns). This miniaturized technology provides for several advantages via process intensification over their contemporary macroscale process equipment counterparts for a large number of industry-relevant applications. The large surface area to volume ratios allowed by this technology (i.e. m²/m³) permit rapid, efficient heat and mass transport. [10] The significantly smaller transport time scales on the microscale mean stronger heat, mass and momentum transport phenomena gradients. These enhanced gradients make processes less wasteful, more efficient, and inherently safer compared to conventional macroscale technology. Generally, the smaller dimensions allow for lower Reynolds number flows (especially in the liquid phase) which gives way to more uniform flow characteristics. This facilitates simpler, more predictable simulations that connect experiment and theory. When there is a better connection between the two, better understandings of systems are developed which allows for maximal process optimization. Parallel architecture can be incorporated to increase production scales and facilitate distribution of process technology [10]. Microtechnology is a relatively new avenue in chemical engineering that has gained popularity in university research increasingly since the dawn of the 21st century.

1.6 Thesis Goals and Contribution to Science

The primary focus of this work is to explore the feasibility of operating a microchannel, high-voltage, nonthermal plasma discharge equipped with a pulsed direct current power supply to drive the conversion of methane into more useful products. Previous research efforts at Oregon State University have employed direct current (DC) electricity as the power source [11]–[13]. The goal of this thesis is to characterize the feasibility and practicality of using pulsed DC as a power source for this chemical process in comparison to previous DC work. The goal of the recent project funded by the Advanced Research Projects Agency- Energy (ARPA-E) at Oregon State University has been to produce more valuable chemical products from a methane feed. The resulting chemistry could fall under the category of GTL if the reactor products contain hydrocarbons with sufficient carbon chains such that they are liquid at ambient conditions (C5+). More valuable gaseous products such as ethylene could fall under the category of GTC since

the added value would come from chemical products that are not necessarily liquid at ambient conditions.

This characterization will include determining process parameters of interest such as chemical conversion, selectivity, and specific energy intensity of product formation. This assessment and interpretation of results will allow for a more complete comprehension of how these microscale processes operate under a wider variety of power electronics applications and the costs/benefits associated with different choices. Thus, it is a contribution to the understanding of how pulsed corona can activate chemical reactions at ambient conditions relative to other methods that procure the same chemistry.

Chapter 2- Background

2.1 Definition of Thermal and Nonthermal Plasmas

Plasmas are comprised of a mixture between charged (ions and electrons) and neutral (radicals and non-ionized atoms/molecules). Imparting a sufficient amount of thermal, electrical, or electromagnetic energy to a gas produces a stream of free electrons, ions and radicals that comprise a fourth state of matter called plasma. Plasmas may be characterized as thermal or nonthermal depending on whether or not the larger ions, radicals and neutral molecules are in thermodynamic equilibrium with the much smaller free electrons. These electrons have a much lower mass $(m_{e^-} = 9.109 \cdot 10^{-31} kg)$ compared to atoms, ions and molecules $(m_{H^+} = 1.673 \cdot 10^{-27} kg)$ and require much less energy compared to any of their equally charged heavier counterparts to acquire a substantial amount of kinetic energy. In essence, this means the plasma is considered nonthermal (or "cold") if the electrons have a much higher temperature ($T_e \ge 10^4 K$) than the gaseous atoms and molecules they are bombarding $(T_g \le 10^3 K)$. Hence, they are not in thermodynamic equilibrium and this fundamental aspect has special implications when it comes to overcoming energy barriers to chemical reactions that would normally require elevated temperatures and pressures sometimes accompanied with expensive catalysts [14].

Nonthermal plasmas, as they are known, are considered to be weakly or partially ionized plasmas. The degree of ionization can be defined as

$$\chi = \frac{n_e}{n_e + n_n} \qquad \qquad Equation \ 1$$

where n_e and n_n are the particle concentrations of electrons and neutral species respectively. Nonthermal plasmas have a degree of ionization on the order of $10^{-4} - 10^{-6}$ [14]. Thus, it can be inferred that the vast majority of particles inside a nonthermal plasma discharge have no net electric charge and neutral radicals that interact with the plasma must play a significant role in reaction kinetics as compared to chemistry directly involving ionic species.

2.2 Chemical Utility of Plasmas

This work examines the usage of microchannel technology to drive chemical reactions at ambient conditions using a high-voltage, nonthermal plasma discharge. Various types of applications involving different types of chemical conversions have been explored using nonthermal plasma. These include (but are not limited to):

- Methane and hydrocarbon reactions
- Destruction of volatile organic compounds (VOCs) and other hazardous compounds
- Ammonia synthesis and nitrogen fixation
- Nanoparticles and material synthesis
- CO₂ and H₂O dissociation

Methane conversion has been the subject of previous research efforts have but there has been a lack of focus on what effect operating parameters and plasma properties have on conversion, selectivity and energy efficiency of this reactive process [13]. Figure 5 shows how high temperature electrons can collide with atoms and molecules to form ions and other product species.



Figure 5: Illustration of elementary processes. a) Ionizations. b) Dissociative attachment and formation of a negative ion. c) Complex ion formation. Taken from [15]

There are several factors that affect the probability of collisions in plasma-chemical systems that lead to ionization, radical formation and subsequent elementary chemical

processes of interest:

- The most fundamental of these quantities is the **reaction cross section** (σ) which can be described as an imaginary circle of area σ comprised of the radii of the two colliding species $\pi (r_1 + r_2)^2$. An elementary reaction takes place if a colliding component crosses the imaginary circle. [16]
- The mean free path (λ) describes how far one collision component travels on average before a collision event occurs. This can be computed using the following where λ_{AB} is the mean free path of A with respect to B, n_B is the number density of species B and σ_A is the cross section of component A. [16]

$$\lambda_{AB} = \frac{1}{n_B \sigma_A} \qquad Equation \ 2$$

 The interaction frequency (γ) of species A with species B can be described as the ratio of their relative velocity (v) to one another to the mean free path. This can also be extended to the velocity distribution function with the cross section as a function of velocity averaged out by integrating over the domain of relative velocities. [16]

$$\gamma_A = \frac{v}{\lambda_{AB}} = n_B \int \sigma(v) v f(v) dv = \langle \sigma v \rangle n_B \qquad Equation 3$$

The reaction rate (ω) is defined as the number of elementary processes that occur per unit volume per time. For a simple system involving two colliding species A & B, this quantity is the product of the interaction frequency of A with B and the number density of A (n_A). [16]

$$\omega_{A+B} = v_A n_A = \langle \sigma v \rangle n_A n_B \qquad Equation 4$$

The reaction rate coefficient (k) for bimolecular reactions is equivalent to (συ) can be expressed as: [16]

$$k_{A+B} = \int \sigma(v)vf(v)dv = \langle \sigma v \rangle \qquad Equation 5$$

Direct ionization by impact of energetic electron species can be classified as dissociative, non-dissociative and stepwise based on the fundamental mechanism involved.

Direct ionization by electron impact occurs when an electron with sufficient energy collides with a neutral species to produce a successful ionization event in one collision. This can be shown for a monatomic species (A): [16]

$$A + e^- \rightarrow A^+ + e^- + e^-$$
 Equation 6

Or similarly as a **non-dissociative impact ionization** event for diatomic species (AB) when the electron energy does not significantly exceed the ionization potential. [16]

$$AB + e^- \rightarrow AB^+ + e^- + e^-$$
 Equation 7

Dissociative impact ionization can occur when the electron energy is much greater than the ionization potential. This can be depicted chemically as follows: [16]

$$AB + e^- \rightarrow A + B^+ + e^- + e^-$$
 Equation 8

Stepwise ionization is a secondary event where a previously excited species undergoes a collision with an energetic electron. This requires higher concentrations of excited neutral species which are present when the electrons and neutrals are closer to thermodynamic equilibrium as would be observed in a so-called "thermal" plasma of high density. The following shows how a stepwise ionization event could occur for species A: [16]

$$e^- + A \rightarrow A^*$$
 Equation 9

$$e^- + A^* \rightarrow A^+ + e^- + e^-$$
 Equation 10

Photo-ionization can occur when a photon of sufficient energy collides with a neutral species. These are generally photons in the ultraviolet and higher energy range of the electromagnetic spectrum. Thermal plasmas are more affected by the photo-ionization phenomenon but it does affect nonthermal plasma behavior to a lesser extent. This can be described chemically as: [16]

$$h\nu + A \rightarrow A^+ + e^-$$
 Equation 11

In addition to ionization events that represent the energy uphill production of charged species from neutrals, recombination and attachment reactions can occur. Positive ions typically undergo reactions involving recombination. **Dissociative electron-ion recombination**, where ion AB⁺ becomes exited and disassociates into A and excited B^{*}, can be described as follows: [16]

$$e^- + AB^+ \rightarrow (AB)^* \rightarrow A + B^*$$
 Equation 12

Three-body electron-ion recombination is when another free electron acts as a "third body partner" and facilitates the recombination of a positive ion into an excited species as shown below: [16]

$$e^- + e^- + A^+ \rightarrow A^* + e^-$$
 Equation 13

Recombination energy can also be released as photons during so-called **radiative** electron-ion recombination. [16]

$$e^- + A^+ \rightarrow A^* \rightarrow A + h\nu$$
 Equation 14

Negative ions can exist in plasmas as well. These tend to occur more so in electronegative gases (i.e. O₂, F₂, Cl₂, etc.). **Dissociative electron attachment** occurs when the products are more electronegative (example below): [16]

$$e^- + AB \leftrightarrow (AB^-)^* \rightarrow A + B^-$$
 Equation 15

Three body electron attachment occurs when the electron energies are not sufficient to procure dissociative attachment (first example below). An important example of this phenomenon in the real world is oxygen anion formation in air via nonthermal plasma (second example below). [16]

$$e^- + A + B \rightarrow A^- + B$$
 Equation 16
 $e^- + O_2 + M \rightarrow O_2^- + M$ Equation 17

Chemical activation of methane involves these plasma-chemical principles. Mechanisms have been proposed in literature for dissociation and ionization. The following are examples of methane ionization by electron impact and their threshold energies in eV from Yuan et al. [17]

12.6 eV
$$CH_4 + e^- \rightarrow CH_4^- + 2e^-$$
 Equation 18

14.3 eV
$$CH_4 + e^- \rightarrow CH_3^+ + 2e^- + H$$
 Equation 19

15.1 eV
$$CH_4 + e^- \rightarrow CH_2^+ + 2e^- + H_2$$
 Equation 20

22.2 eV
$$CH_4 + e^- \rightarrow CH^+ + 2e^- + H_2 + H$$
 Equation 21

25 eV
$$CH_4 + e^- \rightarrow C^+ + 2e^- + 2H_2$$
 Equation 22

The last equation demonstrates how a highly energetic electron could possibly completely dehydrogenate a methane molecule in one step. However, the probability of this occurring in one step is small since the average electron energy in a nonthermal plasma in a 1 mm gap discharge at 700 V is about 5.6 eV. [13] Therefore, in order for observed levels of carbon black formation to occur, the majority of dehydrogenated radicals and ions most likely undergo a sequential series of electron impacts and dehydrogenation events.

Dissociation of methane molecules into neutral radicals is an important mechanism in nonthermal plasma chemistry. Especially since the degree of ionization is rather low in nonthermal plasma. The following are examples of methane dissociation by electron impact and their associated threshold energies in eV taken from Yuan et al. [17]

9 eV
$$CH_4 + e^- \rightarrow \dot{C}H_3 + H + e^-$$
 Equation 23

10 eV
$$CH_4 + e^- \rightarrow CH_2 + H_2 + e^-$$
 Equation 24

11 eV
$$CH_4 + e^- \rightarrow \dot{C}H + H_2 + H + e^-$$
 Equation 25

Threshold energies for dissociation events are lower overall than those required for ionization events. This means these events are more likely to occur in a standard nonthermal plasma electron energy distribution where the average electron energy could be 5.6 eV for methane in the scenario cited previously.

Higher order hydrocarbons can be formed from methane-derived radicals (including metastable CH₂ carbine and CH₃ methyl intermediates) via the following to produce ethylene and ethane. Standard enthalpies at 298 K were taken from Ruscic (2015) and converted to eV. [18]

$$\Delta H_{298K} = -3.90 \text{ eV} \qquad 2 \dot{C} H_3 \rightarrow C_2 H_6 \qquad Equation 26$$

$$\Delta H_{298K} = -7.57 \ eV \qquad 2 \ \ddot{C}H_2 \rightarrow C_2H_4 \qquad Equation \ 27$$

Any reaction with methane liberates hydrogen. The standard enthalpy for diatomic hydrogen formation from Ruscic (2015) is given as: [18]

$$\Delta H_{298K} = -4.52 \text{ eV} \qquad 2 \text{ H} \rightarrow H_2 \qquad Equation 28$$

Since synthesis gas is the major component of the product mix in an actual experiment involving a plasma discharge, methane and carbon dioxide, it would be useful to mention the chemical equation and overall enthalpy of the methane dry reforming reaction. [19]

$$\Delta H_{298K} = +247 \frac{kJ}{mol} \qquad CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad Equation 29$$

The addition of excess CO_2 into the methane stream also oxidizes the solid carbon black that forms as methane reacts in the plasma via the Boudouard reaction. This reaction is endothermic and equilibrium towards carbon monoxide is favored at higher temperatures (>700°C). [20]

$$\Delta H_{298K} = +172 \frac{kJ}{mol} \qquad \qquad C_{(s)} + CO_2 \leftrightarrow 2CO \qquad \qquad Equation 30$$

The electron emitter side of the electrode becomes red hot during plasma operation. This is why having a relatively high proportion of CO_2 in the reactive stream with methane helps quell the carbon black formation that is extremely detrimental to reactor longevity.

The following section will focus on the fundamental physics of plasmas now that the overall fundamental chemistry of nonthermal plasmas has been covered.

2.3 Fundamental Physics & Electrical Behavior of Plasmas

A plasma discharge is formed when an electric potential gradient between two electrodes exceeds the dielectric breakdown threshold for the gaseous species occupying the space between. Electrons gain sufficient energy from the electric field that they are able to overcome the band gap energy barrier. The gas between the electrodes disassociates into a stream of free electrons, ions and radicals once the dielectric breakdown threshold has been exceeded. This occurs via elastic and inelastic collisions where kinetic energy is transferred and redistributed among the species present. Energy required for atoms and molecules to ionize, dissociate and acquire excited energy states comes from this transfer of energy. Nonthermal plasmas have characteristic spectral emission lines that can be used to identify species of interest based on known energy levels for transitions between electronic states. This contrasts with thermal plasmas where high temperatures produce a blackbody radiation profile in the visible light range of the electromagnetic spectrum. Various DC plasma geometries can be described as positive or negative based on the polarity of the electrical configuration. Plasmas have characteristic voltage and current behavior that can be differentiated into distinct regions.

Figure 6 shows the three primary operating regimes for a classical DC electric discharge.



Figure 6: Voltage vs Current behavior for a DC plasma discharge showing the dark, glow, and arc discharge regimes. Taken from [21]

Dark Discharge is the region where the discharge is not visible (A-D). Cosmic rays and other ambient radiation give rise to minimal voltage and current behavior naturally. As the voltage rises, the electrons acquire enough energy to from ions via collisions with neutral atoms, however, these charged species are formed nowhere near the necessary rate to produce a breakdown event known as a Townsend Avalanche. The spark regime is where pulses of repetitive uniformity can form in regions of high current density (D-E). These pulses are a consequence of secondary electron emission. [22] This phenomena tends to cause interference issues with laboratory equipment and other nearby electronic devices.

Glow Discharge is the region where the Paschen breakdown voltage has been exceeded but there is not enough energy present in the system to attain thermal equilibrium between the electrons, ions and neutral species. This voltage is dependent on the pressure and the gap distance and varies depending on the gaseous species present per Paschen's Law. Light is clearly visible in this regime as photons are readily emitted as electrons attain excited energy levels and decay via characteristic quantum spectral emissions. At point E, the ions are bombarding the cathode sufficiently as to release secondary electrons as part of the Townsend avalanche. The glow regime is characterized as having current that is orders of magnitude higher than the spark regime. Unlike the pulsed nature of the spark regime, there is a constant flow of electrons and positive/negative ions. The voltage remains nearly constant as the current increases (F-G). The surface area of the emitting electrode becomes more utilized as the current increases. Eventually, the current becomes high enough that the electrode becomes saturated and thus the voltage must increase in order to provide the necessary driving force to increase the power of the system (G-H). [22]

Arc Discharge is the region where the system is sufficiently saturated with current such that Joule heating occurs as a result of kinetic energy dissipation between the electrons, ions and neutrals (H-K). The wavelengths of visible photons emitted in this regime begin to represent a blackbody radiation profile due to the increased temperatures present. Thermionic emission of electrons becomes dominant as current increases. The voltage decreases as the current increases until the cathode melting point is reached (where the voltage will rise once again). [22] The focus of this work is in the glow discharge region. The heat produced in arc discharge would be considered wasteful and detrimental to the idea of efficiently producing value-added chemicals from methane feedstocks. The spark region is generally avoided experimentally because the transient nature of the electrical behavior makes taking steady, repeatable measurements nearly impossible.

Electromagnetic interference from plasma operation in the spark region can also cause equipment malfunction in the laboratory.

Figure 7 depicts a negative DC corona on an atomic level.



Figure 7: Diagram of a negative DC Corona depicting formation of ions from collisions with electrons in a point-to-plane geometry. Taken from [23]

Plasma electrons also follow Gaussian statistical energy distributions where most electrons will have a mean energy and few electrons will have energies that are much lower or much higher. Thermal plasmas (such as lightning and electric arcs) have local thermodynamic equilibrium as the heavy particles have temperatures that approach those of the much lighter electrons. Temperature differences between these two can be characterized by the square of the ratio of the electric field to the gas pressure (E/p). Local thermodynamic equilibrium occurs at small values of E/p. Such systems in quasiequilibrium can be described using an electron energy distribution function (EEDF) such as the Maxwell-Boltzmann distribution. [16] Since nonthermal plasmas are nowhere near thermodynamic equilibrium with electron temperatures much higher than heavy particles, a different model is required to more accurately represent the plethora of electron temperatures present in this phenomena. This is where other EEDFs commonly used to describe non-equilibrium systems such as the Druyvesteyn distribution come into play. An understanding of these electron distribution functions allows for the quantification of what fraction of electrons have sufficient energy to disrupt chemical bonds. EEDFs that describe electron energies where there is no thermodynamic equilibrium between the electrons and heavier species are crucial in mathematical modeling of plasma-chemical processes involving nonthermal plasmas. [16]

 Table 1 below shows a summation of plasma generation methods from published

 literature.
Character of action	Matter	Type of plasma
Electric Field	Gas	Stationary gas discharge
		plasma
Electromagnetic Wave	Gas	Alternative gas discharge
		plasma
Resonant radiation	Atomic vapor	Photoresonant Plasma
Excitation from chemical	Chemically active mixture	Chemical (flame) plasma
reactions		
Laser	Surface or particles	Laser plasma
Injection of electrons or	Surface or ionized gas	Beam plasma
ions		
Injection of nucleating	Ionized gas	Cluster plasma
vapor		
Injection of dust particles	Ionized gas	Dusty plasma
Ionization by hard	Gas (air) with aerosols	Aerosol plasma
radiation		

Table 1: Methods of plasma generation [24]

The method of generation listed in this table that corresponds with this work would be the electric field generated from a gas that propagates via secondary electron emission. This table shows that this is only one method within a broader category of methods to generate plasma.

2.4 Traditional Technologies for Producing Higher-Order Hydrocarbons from

Methane

Nonthermal plasmas have demonstrated methane coupling to higher-order hydrocarbons without energy-intensive conversion of intermediates such as H₂ and CO synthesis gas (syngas) combined with expensive catalysts via traditional Fischer-Tropsch (FT) synthesis. These processes are carried out at elevated temperatures and pressures and tend to have poor yields [25]. Olefins can also be produced from methanol intermediates. [26] However, direct methanol synthesis from methane is not yet commercially feasible and making methanol from methane involves syngas, catalysts and FT synthesis. [27] The C- H bonds in methane (bond energy = 413 kJ mol⁻¹) exhibit marked chemical stability due to a lack of dipole moment and susceptibility to polarization. Chemically, this means these bonds are difficult to activate in chemical reactions that result in value-added products. [28]

2.5 Review of Other Pulsed DC Methane Conversion Work

There has been plenty of chemical research using pulsed plasma discharge over the years using a wide variety of reactor input mixtures, operating parameters and geometries. [17], [29]–[37]

Table 2 provides a comparison of a select number of papers that have been published relating to the topic of this work.

Author(s)	Zhang et al. (2018)	Yao et al. (2002)	Lotfalipour et al. (2014)	Hoeben et al. (2014)	Yuan et al. (2018)	Zhao et al. (2006)	Ghorbanzadeh et al. (2009)
Reactor Geometry	Coaxial DBD i.d. 25 mm	Coaxial DBD i.d. 12 mm	Coaxial DBD i.d. 40 mm	Corona-over- water	Coaxial DBD i.d. 50 mm	Coaxial DBD i.d. 24 mm	Coaxial DBD i.d. 10 mm
Electrode Geometry	Point-to-plane	Point-to- plane	Point-to-plane	Wire-to-plane	Point-to-plane	Wire-to-plane	Wire-to-Plane
Pulsed DC Frequency	1500 Hz	2000 Hz	1-22 kHz	65 Hz	1-5 kHz	up to 1000 Hz	440 Hz
Voltage	16-20 kV	8-14 kV	15-24 kV	65 kV	12.1-12.9 kV	20 kV	25 kV
Gap Dist.	2.5 mm	4.5 mm	3-9 mm	18 mm	2-10 mm	1.4 mm	9.7 mm
Inlet Chemicals	Pure Methane	Pure CH ₄	Pure CH ₄	CH4, O2, CO2	Pure CH ₄	N ₂ & CH ₄	CH ₄ , O ₂ , Ar
Products of Interest	H ₂ & Higher Hydrocarbons	Acetylene	Higher hydrocarbons	Oxygenated Compounds & Higher Hydrocarbons	Higher Hydrocarbons	Higher Hydrocarbons	Oxygenated Compounds & Higher Hydrocarbons
Inlet Temp	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient
Catalyst	None	None	None	None	None	None	None
Analytics	GC TCD FID	GC FID	GC TCD FID	GC FID MS	GC TCD FID	RGA	GC TCD FID
Conversion	6-9%	15-40%	33-45%	6-20%	30-50%	5-30%	5-30%
Energy Metric ¹	6-7%	9.2 [kWh (kg-C ₂ H ₂) ⁻¹]	30-33%	$\begin{array}{c} 10^{-1} \text{ nmol } J^{-1} \text{ for} \\ C_2 H_4 \end{array}$	12-55%	5-35%	Not investigated
(with basis	(LHV ECE		(LHV ECE		(LHV ECE	(Enthalpy	
remark for % values)	basis)		basis)		basis)	basis)	
Reference	[29]	[30]	[31]	[32]	[17]	[35]	[36]

Table 2: Literature review table for some select works related to pulsed DC methane conversion

¹ Definitions vary

The most common configuration among papers related to the pulsed plasma conversion of methane are coaxial dielectric barrier discharge (DBD). Of the sample of literature surveyed, wire-to-plane and point-to-plane appear to be the most common plasma discharge configurations implemented in this type of research. Gap distances tend to be on the order of millimeters and voltages tend to be in the tens of kilovolts. The duty cycle of the pulsed plasma tends to vary in the literature.

2.6 Potential Benefits of Using Pulsed DC Plasma for Methane Conversion

A plasma that has formed will generally continue to operate in the presence of an external electric field (not counting reactive plasmas with surface coke formation, etc.). If the external field is switched off, the plasma enters a state of decay where the ions recombine and the plasma diffuses spatially back into the ambient gas. This is called the afterglow plasma. [24] The lifetime of ion molecules at atmospheric pressure is less than 100 µs. [31] This period of time would correspond to a frequency of 10 kHz.

Averaging the power input is necessary when assessing a signal that is changing predictably in a cyclic manner. Thus, one benefit of having pulsed power is the ability to attain products associated with a higher power input by using higher bursts of current during each cycle at lower duty ratios. Pulses of a higher energy density in a reactive plasma consisting of CH_4 and CO_2 has been shown to lead to a higher production of synthesis gas (H₂ and CO) compared to higher order hydrocarbons. [38]

Chapter 3- Experimental

3.1 Reactor Design

The microchannel reactor body used in this study was constructed using a piece of glassmica machinable ceramic (also known under brand name Mykroy®). The body of the reactors were of the dimensions 15.5 cm x 3.5 cm x 0.6 cm. These were cut from a larger chunk of material that was purchased in bulk. A point-to-point geometry was implemented to minimize the necessary inception voltage and create a device that could operate independently of polarity choice. This is unlike a point-to-plane geometry which works more optimally when the emitter (point) is negatively charged and the collector (plane) is positively charged. The flow channel and electrode spaces were milled using a CNC machine programmed with simple G-Code. A gap of 500 microns width and depth running the entire length of the flow channel was desired. In order to investigate the effects of higher power input and increased residence time of inlet gas in the plasma, 10 spaces to hold point-to-point discharges in series were implemented along the flow channel. Spacing between electrodes was set at 0.3 inches to allow sufficient distance between each electrode such that they would not interfere with neighboring electrodes. The quantity of 10 was arbitrarily chosen and the effects of multiple discharges in series was not investigated in this work. All experiments in this work involve a single discharge. Inlet and outlet holes were drilled using a 1/16" tap after milling was completed. A 1/4" hole was drilled on the top to enable the reactor to be mounted to the setup. Figure 8 shows a milled reactor body of the dimensions described above.



Figure 8: Labeled photograph of a bare reactor body identifying key components.

Tungsten inert gas (TIG) welding electrodes (CK Worldwide® brand) doped with 2% thorium of 0.020" diameter were cut into 25 mm length segments to serve as the reactor electrodes. Thoriated tungsten electrodes were chosen because the lower work function of thorium facilitates field emissions of electrons from the solid surface. The length was chosen to facilitate the implementation of an alligator clip on the final reactor product. One tip of each segment that was to be inserted into the final reactor was sharpened using a Dremel® 3000. The cut electrodes were inserted into the channels and secured in place with Loctite® 431 instant adhesive. A microscope was used to ensure that the electrodes would be as close of a distance to the 500 micron gap as possible. Figure 9 shows an example of a sharpened electrode glued in place on a reactor.



Figure 9: Thoriated tungsten electrodes in place on a reactor body. The 500 micron wide and deep flow channel runs up and down through the photograph and the electrodes are placed as close to 500 microns apart as possible. The bluish flakes are residual particles of RTV silicon gasket making compound from recycling reactors.

After curing, the excess adhesive would be removed and a 4" x 1" x 1/8" borosilicate window would be placed on top of the electrodes and the reactor channel. The reactor would be sealed with Permatex® blue RTV silicone gasket making compound and allowed to cure overnight. Inlet and outlet 1/16" diameter tubes would be inserted into the back of the reactor and sealed with the RTV compound. After curing, the edges around the electrodes would be reinforced with Loctite® adhesive in order to make the device fully hermetic. Figure 10 shows frontal, lateral, and rear views of the finished reactor product.



Figure 10: Photographs of finished reactor; A) Front of reactor; B) Side of reactor; C) Rear of reactor

The reactor was ready for implementation into the rest of the experimental setup once the

device was confirmed to be fully hermetic via leak testing with gas flow and a soapy

water solution.

3.2 Electrical Circuit

The electrical circuit was driven by a high voltage power supply (Acopian® brand P05HP12 model) with voltage and current maximum ratings of 5 kV and 15 mA respectively. The power supply was placed in series with 2 high power ceramic resistors (Ohmite® brand L100J100KE model 100 k Ω 100 W rating) to provide sufficient ballast resistance to sustain a plasma discharge in the glow operating region (200 k Ω total ballast resistance). A high voltage power NpN MOSFET (IXYS® brand IXTH1N450HV model 4.5 kV 1 A rating) was wired into a circuit with a compatible gate driver (Micrel® brand MIC4452YN model) in order to provide the necessary voltage and current to drive the MOSFET gate. The switching signal was initiated by a voltage pulse from an Arduino® Uno with a simple program to produce voltage pulses at various frequencies. Duty ratio was maintained at 0.5 for the first set of experiments and then changed for the second set of experiments at select frequencies. A digital phosphor oscilloscope (Tektronix® brand DPO5204B model 2 GHz bandwidth 10 GS/s sample rate) was used to assess the voltage and current waveforms in the system. A high voltage differential probe (Micsig® brand DP20003 model 1 M Ω impedance 5.6 kV maximum) was connected with the positive side after the ballast resistor and the negative side connected after the ground side of the switch. The current was estimated using the current monitoring circuit located on the back of the power supply. A standard differential probe for the oscilloscope was used to monitor current on a separate channel by taking the voltage across a 1 k Ω resistor connected on the ground side of the reactor. Figure 11 shows a circuit diagram depicting the power electronics setup used in this work.



Figure 11: Pulsed DC power electronics apparatus used in this work

3.2.1 Arduino, MOSFET & Gate Driver

The Arduino was programmed to send 5 V pulses in various increments to the gate driver to produce a desired frequency. The gate driver had rise, fall, delay-on and delay-off times of 20 ns, 24 ns, 25 ns and 40 ns respectively. The MOSFET had rise, fall, delay-on and delay-off times of 43 ns, 120 ns, 30 ns and 73 ns respectively. This equates to a total circuit turn-on time of 118 ns and turn-off time of 257 ns. This sums to a total delay of 375 ns in each cycle using this particular equipment. It is imperative to take this delay into account when assessing circuit performance.

3.3 Chemical Analytics

A chemical analytics system was implemented in order to be able to precisely set and characterize the chemical composition of the gaseous mixture entering and exiting the reactor system. Figure 12 shows the chemical analytics system that was used in this study.



Figure 12: Diagram of experimental setup used in this study.

Three pressurized tanks (nitrogen, methane and carbon dioxide) were connected to mass flow controllers (MFCs) to dispense specific amounts of each species to the reactor inlet mixture (all Alicat® brand MC-500SCCM-D-PCV10/5M model 200:1 turndown ratio 500 sccm maximum). Pressure was controlled downstream of the reactor using a backpressure regulator (Alicat® brand PCH-100PSIA-D-PCV03.30-2ST/5P model 100 psia maximum). A mass flow meter (Alicat® brand M-2SLPM-D/5M model 2 SLPM maximum flow) was used to help confirm whether the MFCs were working properly and help determine if the system was fully hermetic.

The system outlet was equipped with an SRI 8610C gas chromatograph (GC) equipped with a 1 mL sample loop, switchable valves and two columns in series (Hayesep-D packed column and molecular sieve 13x). Helium was used as the carrier gas. Separated samples would encounter a thermal conductivity detector (TCD) and helium ionization detector (HID) upon exiting the columns. The TCD detector compares the thermal conductivity of the column effluent gas to the thermal conductivity of the carrier gas. The HID detector ionizes a makeup stream of carrier helium gas. Photons from the recombination of these ions then ionize the sample molecules which produce a detectable electrical signal between two electrodes. The TCD was used to quantify the gaseous species present in major quantities (N₂, CH₄, CO₂) and species present in minor quantities (CO) that saturate easily on the HID detector. All other minor species were quantified using the HID detector. Figure 13 shows a photo of the experimental setup in action with the gas chromatograph connected.



Figure 13: A photograph of the cart containing the experimental setup in the laboratory.

3.4 Typical Experimental Procedure

A typical experimental procedure began with baking out the GC for 1 hour at 200°C to eliminate any residual chemical species that might be present in addition to the carrier gas. The gas tanks would be opened and the MFCs would be turned on and set to desired flowrates. The backpressure regulator would be set to slightly above ambient (15.2 psia in this work) to help ensure smooth outflow by providing a little extra pressure to the rest of the system downstream. The temperature of the reactants entering the system were ambient ($\approx 20^{\circ}$ C). The reactive mixture would be allowed to flow and reach steady state while the GC was warming up. A 3:1 molar ratio of CO_2 :CH₄ was chosen with a high abundance of CO₂ necessary to assist in oxidation and removal of carbon black (coke) via the Boudouard reaction. This allows the reactor to continue operating without formation of a carbon coke filament that eventually shorts the circuit and often causes permanent failure of the electrode. Lower ratios of CO₂:CH₄ result in excessive formation of coke that would cause quick failure of the reactor (even if using a fresh electrode). The GC was programmed to allow the entire sample to enter the Hayesep-D column at 50°C. A stop flow solenoid would be activated once the lighter species (H_2, CO, N_2, O_2) had eluted to stop flow within the Hayesep-D column (just after 2 minutes in this particular setup). The lighter species would make their way through the Molecular Sieve 13x and be separated to a degree sufficient to quantify. Around 10 minutes (after the lighter species had eluted): 1) the solenoid was opened; 2) the valve was turned back; and 3) the temperature was ramped to 190°C at a rate of 20°C/min to allow the heavier species (CH₄, CO₂, C₂, C₃ and higher order species) to elute.

The oscilloscope was configured with the high voltage differential probe as the input in one channel to monitor the reactor voltage. One lead would be placed on the ground side of the ballast resistor and the other lead would be placed on the ground side of the MOSFET switch. Current was monitored on a separate channel by placing leads across a 1 k Ω resistor. This configuration is shown in Figure 11 above.

Each run consisted of 2 GC samples: a baseline and a plasma sample. The baseline was taken without any plasma first to show the GC output when there was a reactive mixture but no reaction. For a plasma sample, the power supply would be switched on and the plasma discharge would be allowed to operate. Voltage and current would be adjusted until the desired operating voltage/current would be reached on the oscilloscope display. A stopwatch would be used once this power level had been reached and the reactive system would be allowed to operate for a minimum of 45 seconds (at a flow rate of 40 sccm in this work). This was to ensure that 1) any dead volume in the system from the plumbing would be occupied with the reacted mixture and 2) the 1 mL GC sample loop would also contain this mixture upon switching the valve. Oscilloscope screenshots would be collected during plasma operation to record snapshots of the electrical behavior in the circuit. The oscilloscope was configured to display averaged values of current and the high/low. The power supply was shut off after the GC sample was taken and the results would be recorded once the sample had eluted. Integrated GC signals over time would be converted to volume percentages using calibration curves. An assumption of ideal gas behavior was made to equate volume to mole percent. These values were then used to calculate derived quantities and their respective uncertainties.

3.5 Methods of Data Analysis

The following equations define parameters that were calculated from collected experimental data where \dot{n} is the molar flow rate for the specified species.

Conversion of CH₄

$$C_{CH_4} = \frac{mol \ CH_4 \ reacted}{mol \ CH_4 fed} = \frac{\dot{n}_{in} - \dot{n}_{out} \left(\frac{mol}{s}\right)}{\dot{n}_{in} \left(\frac{mol}{s}\right)}$$
 Equation 31

Selectivity toward C₂+ for x = (2, 3, 4, ...)

$$S_{C_2^+} = \frac{\sum x \cdot \dot{n}_{C_x}}{mol \ CH_4 \ reacted} = \frac{\sum x \cdot \dot{n}_{C_x} \left(\frac{mol}{s}\right)}{\dot{n}_{in} - \dot{n}_{out} \left(\frac{mol}{s}\right)}$$
Equation 32

Yield C₂+

$$Y_{C_2^+} = C_{CH_4} \cdot S_{C_2^+} = \frac{\sum x \cdot \dot{n}_{C_x}}{mol \ CH_4 fed} = \frac{\sum x \cdot \dot{n}_{C_x} \left(\frac{mol}{s}\right)}{\dot{n}_{in} \left(\frac{mol}{s}\right)}$$
 Equation 33

Specific Energy Intensity of Compound A

$$SE_A\left(\frac{kJ}{mol}\right) = \frac{Energy\,Input\,Rate\left(\frac{kJ}{s}\right)}{rate\,mol\,A\,produced\left(\frac{mol}{s}\right)}$$
 Equation 34

Specific Energy Intensity of Synthesis Gas² [39]–[41]

$$SE_{syngas}\left(\frac{kJ}{mol}\right) = \frac{Energy\ Input\ Rate\ \left(\frac{kJ}{s}\right)}{rate\ mol\ (H_2+CO)_{produced}\left(\frac{mol}{s}\right)}$$
 Equation 35

² Definition taken from literature

Propagation of Uncertainty for f(x, y, z, ...)

$$s_f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 s_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 s_y^2 + \left(\frac{\partial f}{\partial z}\right)^2 s_z^2 + \cdots} \qquad Equation \ 36$$

A greater amount of moles of gas exit the reactor than enter the reactor due to stoichiometry. The plasma discharge disrupts the chemical bonds in methane and carbon dioxide causing chemical reactions to occur. The GC sample loop used in this study holds 1 milliliter. This corresponds to a fixed number of gas molecules at any given temperature and pressure per the ideal gas law (deviation from ideality is minimal at ambient conditions). It is necessary to account for this change by introducing an inert internal standard. Nitrogen was chosen in this case due to its abundance and the stability of its triple bond. Nitrogen has been known to react in plasma discharge but is assumed to react negligibly using the parameters in this work. A scaling factor was defined to adjust the estimated output molar flow rates based on the assumption that any nitrogen gas reactions were negligible:

$$\alpha = \frac{\text{measured } N_2 \text{ mol input rate}}{\text{measured } N_2 \text{ mol output rate}} \qquad Equation 37$$

This would be used in a calculation to scale the output number of moles as shown here for conversion:

$$C_{CH_4} = \frac{\text{mol } CH_4 \text{ reacted}}{\text{mol } CH_4 \text{ fed}} = \frac{\dot{n}_{in} - \alpha \cdot \dot{n}_{out}}{\dot{n}_{in}} \qquad \qquad Equation \ 38$$

Chapter 4- Results and Discussion

4.1 Characterization of Plasma Discharge

The IV behavior of the plasma must first be characterized to ensure the experiment is operating in the glow regime. Figure 14 shows an IV curve that was created using the experimental setup.



Figure 14: IV Curve of the reactive mixture

This curve was created by starting with the current at zero and turning it up slowly and recording the voltage on the oscilloscope using the high voltage differential probe. Clearly, the discharge requires about 2,000 V to initiate and about 480 V to operate. Starting the plasma with high current and slowly adjusting it lower results in the hysteresis shape shown in the background (Figure 6). This mode of operation, however, was not stable and was more difficult to measure than the low-to-high method. The breakdown voltage was consistent among runs as the discharges in the reactor were changed due to excessive carbon coke formation. This voltage is dependent on the ambient pressure and the distance between the electrodes as correlated by Paschen's Law. The consistency in the breakdown voltage observed among various electrode pairs in the reactor meant that the variance in electrode spacing was small.

4.2 GC Chromatogram Baseline and Plasma

Each run consisted of collecting a chromatogram that consisted of no reaction (baseline) and a reaction (plasma) for the TCD and the HID detectors. Figures 15 and 16 show a baseline and plasma run for the HID detector.



Figure 15: Baseline chromatogram for a straight DC experimental run (0 Hz).



Figure 16: Plasma chromatogram for a straight DC experimental run using HID detector (0 Hz) The peaks for C3 and higher products are quite small and difficult to make out unless a zoomed plot is featured. Figure 17 shows the plot zoomed in to an x-axis window of 18.5 to 30 min and a y-axis window of 0 to 30 mV.



Figure 17: Plasma chromatogram for a straight DC experimental run (zoomed in to show higher order hydrocarbon products) using HID detector (0 Hz)

The amount of C3 and C4 products made is quite miniscule so they were not considered for the energy balance. The most productive runs produced no more than 0.02-0.03 vol% C3 and 0.002-0.01 vol% C4. This varied greatly between runs due to such incredibly small amounts being produced. Similarly with ethylene, production amounts trended between 0.25-0.5 vol%. Ethylene production was quite variable even though it was about an order of magnitude higher than production of C2 and C3, yet it was still quite insignificant compared to the amount of synthesis gas produced by this process. Production of H₂ and CO was dominant and ranged from about 4.5-6.0 vol% and 3.7-7.2 vol% respectively.

The TCD detector was used to quantify the major components of the gaseous mixture. Figure 18 shows a baseline and plasma chromatogram superimposed over each other as two separate series on the same plot.



Figure 18: Baseline and Plasma chromatogram for a straight DC experimental run shown using the TCD detector. A decrease in reactants and formation of CO is shown for the plasma being on.

4.3 Nitrogen Scaling and Mass Balance

It is necessary to quantify potential error in the mass balance in any experiment. The number of moles is not conserved due to chemical stoichiometry. A scaling factor mentioned previously was used as a way to help account for this change in moles. In addition, carbon black formation represents a portion of mass entering the reactor that will not be detected by any gas-based chemical analytics used in this study. Figure 19 shows a carbon black filament that formed during operation of the plasma discharge that ended in electrode failure due to formation of a short circuit.



Figure 19: Photograph of reactor showing a carbon black filament that forms and causes a short circuit between the electrode pair and failure of the device to maintain plasma discharge. The right electrode is the emitter and the left electrode is the collector.

Performing a qualitative mass balance on the reactor, it can be inferred that overall:

mass out = mass in - carbon black accumulation

There are only four elements present: 1) carbon, 2) nitrogen, 3) oxygen and 4) hydrogen. Nitrogen was assumed to be inert and the number of moles detected exiting the reactor were scaled so the nitrogen input and output values would be equal (discussed previously). Carbon was known to be lost in the gas phase via the formation of solid carbon black as pictured above. Hydrogen was not able to be fully quantified due to: 1) a lack of knowledge of how the hydrogen distributed among C2 and C3 products (some of which may be unsaturated); and 2) no quantification of H₂O in the output. Oxygenated compounds except for H₂O exiting the reactor were able to be quantified by the GC. Formation of oxygenated organics was assumed to be negligible.

An atomic species balance can be performed to investigate the consistency of the GC performance throughout the experiment. Figures 20 and 21 show the average percent change of carbon, nitrogen and oxygen detected between the baseline and plasma runs as quantified using the HID and TCD detectors of the GC. Figure 20 is using the N₂ scaling factor and Figure 21 is without the N₂ scaling factor.



Figure 20: Average percent change of carbon, nitrogen and oxygen between baseline and plasma runs. These numbers are adjusted using the nitrogen scaling factor so there is no change in the amount of nitrogen because this is enforced.



Figure 21: Average percent change of carbon, nitrogen and oxygen between baseline and plasma runs. These numbers are not adjusted using the nitrogen scaling factor and are based on raw data.

The percent change detected between baseline and plasma runs varies based on a

multitude of factors. There is a different product distribution at the lower frequencies that

favors synthesis gas production (discussed below). This appears to cause less of a variation in the carbon and oxygen balances in absolute magnitude but in the opposite direction. Other variance can be described by: 1) molar dilution, 2) variance in the plasma discharge during experimental operation, 3) calibration error, 4) instrumental response drift over time, 5) natural instrumental noise and 6) minor nitrogen reactivity (in the case involving the N_2 scaling factor).

Molar dilution is primarily why all the percent changes without any N₂ scaling factor are negative. As discussed above, the molar flow rate leaving the reactor is higher than the molar flow rate entering the reactor due to stoichiometry. The 1 mL sample loop samples the same number of moles at the same temperature and pressure. Therefore, the difference in the raw measurements of what is going on before and after the plasma reaction are always going to show a net decrease in atomic species detected.

All results reported in this work are reported using the nitrogen scaling factor.

4.4 Overall Experimental Results

A sweep of various operating frequencies was performed using an average power of 3.1 W. This was the average of the power dissipated across the plasma discharge over time. This represents spurts of 6.2 W of power that average out to 3.1 W overall with the plasma being off half of the time. This was necessary in order to produce repeatable behavior in the plasma.

Figures 22 and 23 show pie charts that depict the distribution of chemicals during the baseline and plasma runs.



Figure 22: Distribution of chemicals in the reactive mixture without plasma.



Figure 23: Distribution of chemicals in the reactive mixture with plasma at 0 Hz.

It is also useful to show a pie chart depicting a different frequency of operation where the distribution of chemicals after interacting with the plasma was slightly different. Figure 24 shows a chart for a 60 Hz run.



Figure 24: Distribution of chemicals in the reactive mixture with plasma at 60 Hz.

At lower frequencies, the plasma had sufficient time to turn off before being reignited. At higher frequencies, the behavior of the plasma started trending towards that of straight direct current. Figure 25 shows results for the conversion, selectivity and yield at the various frequencies explored in this study using a duty ratio of 0.5.



Figure 25: Conversion, Selectivity and Yield for various frequencies at a duty ratio of 0.5 and an average power input of 3.1W. Error bars are to one standard deviation of uncertainty

The conversion does not significantly change between runs. This is because the total average power was kept constant throughout the experiment. However, there is a clear trend in selectivity towards higher hydrocarbons at lower frequencies. This happens where the cycle is sufficiently long such that the plasma has ample time to turn off before being reignited. It can be inferred that using pulses of higher power that average to a constant value over time leads to higher production of synthesis gas and less selectivity towards higher order hydrocarbons. Figure 26 shows an oscilloscope reading at 60 Hz that illustrates how the pulses of higher power can average to a constant value over time.



Figure 26: Screenshot of oscilloscope with plasma on at 60 Hz during experiment

The yellow channel is the voltage reading for the high voltage differential probe connected between the ballast resistor and ground side of the MOSFET switch with 2000x attenuation. The **purple channel is the voltage reading across a 1 k** Ω resistor located on the ground side of the MOSFET switch. This allows for simple computation of the corresponding current as the numerical value shown in volts is equivalent to the numerical value of the circuit current in milliamps (via Ohm's law V=IR). These physical oscilloscope connections are shown earlier in Figure 11 in the experimental chapter of this work. A derived value was added to couple the data from the two oscilloscope channels and show the estimated live power reading (shown in red). In Figure 26, it can be inferred that the average current is displayed at about 6.5 mA but the pulses of current at the duty ratio of 0.5 are valued at about 13 mA. The reactor voltage when the plasma is on is around 470 V (equivalently 235 mV * 2000). This is in good agreement with the voltage in the glow regime in the IV curve shown in Figure 14. Therefore, a profile of higher-powered plasma reactor products can be shown using an overall lower average power. Synthesis gas production is favored at these higher current levels due to the increased probability of collisions between electrons and reactant molecules which leads to overall lower energy products being formed (syngas vs higher order hydrocarbons).

The discharge tended towards direct current operation as the frequency was increased beyond the 10 kHz range. Figure 27 shows an oscilloscope screenshot at a frequency of 10 kHz during plasma operation:



Figure 27: Oscilloscope screenshot of discharge operating at a frequency of 10 kHz.

The switching behavior is clearly present where the short current spike represents the plasma ignition when the switch turns on and the current fall occurs simultaneously with the voltage rise when the switch is off. This contrasts with the less stable behavior observed at 50 kHz as the switch times start becoming too short for the plasma to fully dissipate between cycles. This is shown in Figure 28.



Figure 28: Oscilloscope screenshot showing plasma operation at 50 kHz (derived power trace not present in all screenshots shown in red).

The switching behavior is less pronounced at 50 kHz versus 10 kHz. This is because 1) the physical limitations of the semiconductor driver/MOSFET switching apparatus used in this work are being reached and 2) the plasma is not fully recombined when the switching occurs. Figure 29 shows some of the transient behavior observed due to voltage instabilities created by Trichel pulses during operation in the spark regime.



Figure 29: Oscilloscope screenshot at 50 kHz showing transient voltage behavior due to sparking and electromagnetic interference.

Transient sparking behavior shown made measurement of a stable corona more difficult.

Measurements were not taken unless a quasi-steady state had been reached for at least

one minute to make sure the sample loop was filled with a consistent mixture of gases.

A run was attempted at 250 kHz. The waveform at this frequency is shown in Figure 30.



Figure 30: Oscilloscope screenshot for operation at 250 kHz.

It is clear that there is no significant difference in operation from direct current lacking any switching mechanism. The ripples in current every 2 μ s represent the times the switch is changing between on/off modes. This is due to the fact that the apparatus is switching so fast that the device does not have any time to actually turn on or off. The data obtained for the direct current (0 Hz) and 250,000 Hz runs were similar enough to corroborate that the system could not physically perform any level of adequate switching at this frequency.

A sweep of the effect of duty ratio on conversion, selectivity and specific energy intensity was performed at frequencies of 1 kHz and 10 kHz. Keeping the power constant was difficult to control so the average current was kept at 5 mA for the 0.25 and 0.75 duty

ratio runs. Data from the 0.5 runs for these frequencies was added for comparison. Figure 31 shows the key results from this experiment.



Figure 31: Results of duty ratio sweep at 1 kHz and 10 kHz frequencies with average power input. Conversion, selectivity and yield variables of each frequency are grouped together to show trends easier. Error bars are to one standard deviation of uncertainty.

Conversion was slightly lower at 0.25 and 0.75 duty ratio for both frequencies compared to 0.5 duty ratio. This could be due to the fact that the average power was lower during the 0.25 and 0.75 at 5 mA average current. Selectivity increased at higher duty ratios because the discharge had a lower operating current as its behavior approached that of direct current at higher duty ratios as it was spending 75% of the time being on each cycle. As mentioned previously, the instantaneous current is higher during the lower frequency runs because the metric being considered was average power over all cycles. Yield, the product of selectivity and conversion, was highest at 10 kHz at 0.5 duty ratio.
Marginal benefits in selectivity and conversion appear to be at 10 kHz where the performance of the pulsed plasma discharge starts to trend towards straight direct current. The primary products of this process are synthesis gas with slight amounts of higher-order hydrocarbons that are predominantly ethane and ethylene. Synthesis gas and ethylene are industrially useful products. Therefore, it is useful to discuss how much energy goes into the production of each of these chemicals in this process. Figure 32 shows the specific energy intensity for synthesis gas (SE_{syngas}) and ethylene ($SE_{c_2H_4}$) obtained for each frequency that was tested using the experimental apparatus.



Figure 32: Specific energy intensity for ethylene and synthesis gas plotted versus frequency of plasma discharge operated at 0.5 duty ratio. Error bars are to one standard deviation of uncertainty

The specific energy intensity of synthesis gas ranged from 790. \pm 56.0 kJ mol⁻¹ at 10 kHz to 1,120 \pm 105 kJ mol⁻¹ at 250 kHz. The specific energy intensity of ethylene ranged from 19,660 \pm 4800. kJ mol⁻¹ at 10 kHz to about 34,900 \pm 9,990 kJ mol⁻¹ at 500 Hz. These trends follow the trend in selectivity versus frequency shown in Figure 25 above due to

the pulses of higher power density driving the products more toward synthesis gas at lower frequencies. The large variance in the ethylene volume percent relative to its average value propagated through the experiment. This explains why there is a large variance observed in the energy intensity estimate.

Similarly, this assessment was performed from the data acquired during the duty ratio sweep at 1 kHz and 10 kHz frequencies. This can be seen in Figure 33.



Figure 33: Specific energy intensities for ethylene and syngas at 1 kHz and 10 kHz frequencies using duty ratios of 0.25 and 0.75. Error bars are to one standard deviation of uncertainty. The specific energy intensity for synthesis gas ranged from 654 ± 63.1 kJ mol⁻¹ at 10 kHz 0.25 duty ratio to $1,680 \pm 151$ kJ mol⁻¹ at 10 kHz 0.5 duty ratio. The specific energy intensity for ethylene ranged from $19,660 \pm 4,800$ kJ mol⁻¹ at 10 kHz 0.5 duty ratio to $42,840 \pm 12,360$ kJ mol⁻¹ at 10 kHz 0.75 duty ratio. The trends are less clear than they are in the previous figure showing a frequency sweep at constant power and duty ratio.

Higher duty ratios appear to have opposite effects on the specific energy intensity for ethylene but the error bars are so high that it is hard to discern this from mere experimental error. The specific energy intensity for synthesis gas is lower at lower duty ratios because these runs consist of spurts of higher current that average out over time to the desired power input parameter. There appears to be marginal gains in selectivity, conversion and specific energy intensity overall around 10 kHz at 0.5 duty ratio.

A chemical bandwidth study from the U.S Department of Energy lists the overall specific energy intensity of ethylene to be around 460.5 kJ mol⁻¹. [42] This number is overall much lower than the values observed in this experiment that tended to be around 22,000 kJ mol⁻¹. Pacheco et al. reported a specific energy intensity for synthesis gas to be 88.6 kJ mol⁻¹ using a "warm plasma" process involving a macroscale plasma jet that expands through a complex column. [39] This was much lower than the values observed in this experiment that were between 500-700 kJ mol⁻¹ on average. These values are more in line with experimental data (1,798 kJ mol⁻¹ [43] and 1,134 kJ mol⁻¹ [41]) collected using a more typical corona discharge. Parameters chosen in this experiment were not focused on delivering maximum efficiency. Inefficient glow mode region operation was chosen to make experiments repeatable and provide data with discernable trends. Using pulsed direct current to generate plasma does not improve selectivity to higher order hydrocarbons. Conversion remains constant at the same power level over all frequencies. The ratio of H₂/CO is also an important metric to consider when discussing synthesis gas

production. Especially since the specific energy intensity parameter is calculated based

on the total number of moles of CO and H_2 produced (as defined previously). Figure 34 shows the ratio of calculated molar flow rates exiting the reactor for H_2/CO .



Figure 34: Ratio of H_2/CO molar flow rates exiting the reactor. Error bars are to one standard deviation of uncertainty.

Production of hydrogen is favored using direct current and higher frequencies. The higher power density of the energy pulses at lower frequencies induces carbon monoxide formation. This may be due to the occurrence of the Boudouard reaction near the surface of the electrode between CO₂ molecules interacting with the solid carbon black accumulating on the surface. The splitting of CO₂ molecules at these frequencies explains why there could be an excess of CO compared to H₂. As mentioned previously, the equilibrium in this reversible reaction is shifted towards CO production favored at higher temperatures. The surface of the emitter electrode has been demonstrated to become incandescently hot during operation of the plasma discharge. This becomes more pronounced when the system is operating at higher current levels. The overall H₂:CO ratio produced from plasma dry reforming in a 3:1 molar feed ratio of CO₂:CH₄ has been shown to be less than unity experimentally for a range of various operating conditions in various publications. [38], [44]

Additionally, the water-gas shift (WGS) reaction between H_2 and CO_2 may be involved in this case. The reaction is exothermic and favors CO and H_2O conversion at lower temperatures. There has been an H_2O peak observed in the GC analysis but no calibration was performed and it was not included in any mathematical analysis of the data. This is due to the difficulty of making accurate mixtures of water vapor and other gases given the nature of the water liquid-gas phase equilibrium at ambient conditions near sea level. Water will condense beyond its saturation point which can cause malfunction of the GC if this occurs inside the sample loop or any packed/capillary separation column itself.

There also may be discrepancies in the hydrogen and carbon monoxide values due to calibration errors as well. These two species were calibrated using a syringe to extract gas from a Tedlar® gas sampling bag and pulling in ambient air to dilute the mixture to a desired volume percentage. Human error makes this method less accurate than attaching a pressurized tank to an MFC and adjusting the setpoint to produce a desired dilution of gases at known volume percentages. However, most runs had volume percentages that added up to about 101-103%. Calibrations for each species were performed during completely separate runs. Therefore, if the sum of the volume estimates is within 1-3% of 100%, then the calibrations are consistent and the amount of error present is not excessive. However, minor discrepancies in estimates of product gases produced in

relatively small quantities (compared to the bulk composition) can propagate through calculations and have a profound effect on a final derived value.

4.5 Note on Power Estimation Technique

There was a pronounced difference between the lag times between the voltage and current monitor probes. This can be seen in Figure 35 below.



Figure 35: Oscilloscope screenshot during plasma operation at 1 kHz and 0.25 duty ratio showing difference between voltage and current lag times

This difference occurred because the high voltage differential probe is connected to the active power source while the current monitoring probe across the resistor was a completely passive measurement. The power supply recharges to the higher voltage when the switch is turned off and that internal capacitance of the system is reflected in the

longer rise time. The reading on the current rises and reaches steady operation much faster than the reading on the voltage. The passive measurement is more reflective on what is actually going on in the reactor at any instant so the voltage across the reactor was assumed to be around 480 V for actual discharge power estimation during steady current operation at higher frequencies and lower duty ratios.

Figure 36 shows an oscilloscope screenshot where the fall time of the current was estimated during plasma operation.



Figure 36: Oscilloscope screenshot at 1 kHz and 0.75 duty ratio showing an estimated rise and fall time for the current in the circuit.

The fall time of the current was estimated to be about 20 µs. This is much shorter than the

rise time of the voltage. The rise time of the voltage is shown in Figure 37.



Figure 37: Oscilloscope screenshot at 1 kHz and 0.75 duty ratio showing the voltage channel only and the estimated rise time of the voltage.

The rise time of the voltage was approximately 110 μ s. This is 5.5 times higher than the fall time of the current. As stated previously, this is because the high voltage differential probe is connected to an active power source and the standard differential probe connected across the 1 k Ω resistor to estimate current is a completely passive circuit element. A completely passive measurement is more descriptive of what is going on in the plasma discharge in the reactor since that is also a passive circuit element as well. This is why power calculations assumed the voltage across the discharge gap was already at the typical operating voltage before the extra time had elapsed such that the high voltage differential probe gave the same reading as the reactor voltage. If the current has already reached its operational value, then at that same instant, the voltage across the

reactor has reached its corresponding voltage as estimated by the IV curve in Figure 14 earlier. The power supply charges and discharges every time the MOSFET switches and causes the electricity to pulse.

Chapter 5- Conclusion

5.1 General Remarks

The purpose of this work was to assess whether pulsed direct current is a better way to drive methane conversion towards higher order hydrocarbons. It was necessary to have carbon dioxide present in the stream as an oxidant due to the detrimental effects of coke formation on reactor performance. Pulsed direct current lowers selectivity at frequencies below 10 kHz. Performance begins to match that of direct current if the frequency of pulses increases beyond 10 kHz. Adjusting the duty ratio shows the same decrease in selectivity towards higher hydrocarbons at lower duty ratios. Again, this is because there are shorter spurts of higher instantaneous power that average out over all cycles to a constant value. Higher current increases the amount of electron impact ionization and dissociation events. Having a greater quantity of these events means that more reaction events will occur and products will be shifted towards lower energy products. Higherorder hydrocarbon products that may have formed at the higher currents have a greater chance of being transformed into lower energy synthesis gas alternatives. Thus, pulsed direct current is not a good choice if the goal is to promote formation of higher-order hydrocarbons using this type of process.

5.2 Future Work

One possible future direction for this work could be the implementation of tandem switching with a more complicated MOSFET apparatus. The Arduino in this setup works by switching voltage signals to two ports in tandem. Port 6 turns on while port 7 turns off and vice-versa. This setup could be extended to investigate the effect of numbering up discharges in series by having an adjacent discharge turn on when one turns off. This could potentially have the benefit of added overall methane conversion associated with longer residence times with similar effects on the selectivity towards higher-order hydrocarbons observed in this work.

Exploring parameters that affect energy-related variables is another consideration that must be made in future work. The specific energy intensities reported in this work were significantly higher than values reported by some other research works and industrial government reports. The process must be made more efficient in order for this process to be competitive commercially.

Appendix

A.1 GC Calibrations

The following figures show calibrations that were performed using the SRI-8610C Gas Chromatograph equipped with the TCD and HID detectors for the various species in this study. Intercepts were forced to be zero on each calibration. Many HID calibrations are not linear fits due to the sensitivity of the detector and ease of saturating the signal.

Pressurized tank were connected to an MFC to produce dilutions of the various gaseous species used in this work in order to perform calibrations. Triplicates of each dilution were taken to enable statistical analysis. Hydrogen and carbon monoxide were calibrated by filling a Tedlar® gas sampling bag using pressurized tanks located in an adjacent laboratory. The gas was extracted using a syringe and injected directly into the GC for analysis.



Figure 38: Methane calibration on the TCD detector



Figure 39: Carbon dioxide calibration on the TCD detector.



Figure 40: Nitrogen calibration on the TCD detector



Figure 41: Carbon monoxide calibration on the TCD detector.



Figure 42: Hydrogen gas calibration on the HID detector



Figure 43: Ethylene calibration using the HID detector



Ethane HID

Figure 44: Ethane calibration using the HID detector



Figure 45: Propane calibration using the HID detector



Figure 46: Butane calibration using the HID detector

A.2 Arduino Code

Below is the Arudino code that was used to drive the MOSFET.

```
void setup() {
    // put your setup code here, to run once:
    DDRD = B11111110; // sets Arduino pins 1 to 7 as outputs, pin 0 as input
    void loop() {
    int x = 750 ; // input frequency here
    int y = 250 ;
    delayMicroseconds(x);
    PORTD = B10101000; // Sets 7 high and 6 low
    delayMicroseconds(y);
    PORTD = B01010000; // Sets 6 high and 7 low
```

Figure 47: Arduino code for adjustable duty cycle ratio. Here the period is 1 ms corresponding to a frequency of 1 kHz at a duty cycle of 75%. Variable 'x' tells port 6 how long to pulse the voltage on and variable 'y' tells how long to remain off.

```
void setup() {
    // put your setup code here, to run once:
DDRD = B1111110; // sets Arduino pins 1 to 7 as outputs, pin 0 as input
}
void loop() {
    // put your main code here, to run repeatedly:
    int x = 1 ; // input frequency here
    delay(x); // milliseconds
    PORTD = B10101000; // Sets 7 high and 6 low
    delay(x);
    PORTD = B01010000; // Sets 6 high and 7 low
}
```

Figure 48: Arduino code for a duty cycle ratio of 50%. Variable 'x' defines how long port 6 will turn on and turn off the voltage each cycle. Delay(x) outputs in milliseconds. Here the period is 2 ms for a frequency of 500 Hz.

A.3 Oscilloscope Waveforms

The following are Arudino Waveform screenshots from the oscilloscope used in this work.

A.3.1 Arduino Input Signals at 0.5 Duty Ratio



Figure 49: Arduino Input Waveform for 60 Hz at 0.5 duty ratio





Figure 50: Arduino Input Waveform for 500 Hz at 0.5 duty ratio



Figure 51: Arduino Input Waveform for 1000 Hz at 0.5 duty ratio



Figure 52: Arduino Input Waveform for 5000 Hz at 0.5 duty ratio



Figure 53: Arduino Input Waveform for 10000 Hz at 0.5 duty ratio



Figure 54: Arduino Input Waveform for 50000 Hz at 0.5 duty ratio



Figure 55: Arduino Input Waveform at 250000 Hz at 0.5 duty ratio

A.3.2 Arduino Input Signals at 0.25 Duty Ratio



Figure 56: Arduino Input Waveform at 1000 Hz at 0.25 duty ratio



Figure 57: Arduino Input Waveform at 10000 Hz at 0.25 duty ratio



Figure 58: Arduino Input Waveform at 1000 Hz at 0.75 Duty Ratio



Figure 59: Arduino Input Waveform at 10000 Hz at 0.75 duty ratio

A.4 Sample Calculations

Some sample calculations are necessary to provide a better understanding of how some derived quantities were computed in this study.

A.4.1 Plasma Residence Time Estimation

The flow rate used in this study was 40 sccm. V is the plasma volume, \dot{V} is the volumetric flow rate and τ_{res} is the residence time of the gaseous mixture in the plasma.

$$\dot{V} = 40 \ sccm \left(\frac{1\ min}{60\ s}\right) \left(\frac{1\ m}{100\ cm}\right)^3 = 6.67 \cdot 10^{-7} \ \frac{m^3}{s}$$

Assuming a perfectly cubic reactive volume around the electrode with one side of the cube at 0.5 mm (for mathematical simplicity).

$$V = (0.5 mm)^3 \left(\frac{1 m}{1000 mm}\right)^3 = 1.25 \cdot 10^{-10} m^3$$

$$\tau_{res} = \frac{V}{\dot{V}} = \frac{1.25 \cdot 10^{-10} \ m^3}{6.67 \cdot 10^{-7} \ \frac{m^3}{s}} = 1.87 \cdot 10^{-4} \ s \cdot \left(\frac{1000 \ ms}{1 \ s}\right) = 0.187 \ ms$$

This corresponds to a frequency of $\frac{1}{1.87 \cdot 10^{-4} s} = 5350 Hz.$

The actual residence time is some fraction of this estimate because the plasma discharge is clearly not uniform and does not occupy the complete cubic volume encompassing the 0.5 mm diameter electrodes. Thus, if the actual residence time is 50% of this estimate, this would correspond to a frequency of 5350 $Hz \cdot 2 = 10700 Hz$

At any frequency above this threshold, the pulsing time is lower than the residence time of the gas in the plasma discharge zone. A.4.2 Molar Flow Rate Estimation

The following will qualitatively demonstrate how a molar flow rate is calculated from the GC signal.

First, the peaks are integrated by the GC software and then multiplied by the fitted equations derived from the calibrations to obtain a volume percentage of species A in the mixture.

$$(integrated \ GC \ peak \ area)_A * (calibration)_A = (vol\%)_A$$

The volume percentage of compound A is scaled by the total flow rate to obtain the volumetric flow rate specific to compound A.

$$(vol\%)_A * (total volumetric flow rate) = (vol flow rate)_A$$

All gases have a fixed molar density at a given temperature and pressure per the ideal gas law. Therefore the molar flow rate can be obtained by multiplying the volumetric flow rate by the molar density.

> $(vol flow rate)_A * (molar density ideal gas @ ambient T & P)$ = $(mol flow rate_A)$

A.4.3 Propagation of Uncertainty

The following will demonstrate how a typical uncertainty value was computed for this experiment using the formula:

$$s_f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 s_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 s_y^2 + \left(\frac{\partial f}{\partial z}\right)^2 s_z^2 + \cdots}$$

The quantity used for this demonstration will be the ratio of molar flow rates of H₂:CO defined using variable R:

$$R = \frac{n_{H_2}}{n_{CO}}$$

Applying the formula to R:

$$s_{R} = \sqrt{\left(\frac{\partial R}{\partial n_{H_{2}}}\right)^{2} s_{n_{H_{2}}}^{2} + \left(\frac{\partial R}{\partial n_{CO}}\right)^{2} s_{n_{CO}}^{2}}$$

Taking derivatives:

$$\frac{\partial R}{\partial n_{H_2}} = \frac{1}{n_{CO}} ; \frac{\partial R}{\partial n_{CO}} = \frac{-n_{H_2}}{n_{CO}^2}$$

Applying derivatives to s_R (negative term is canceled when squared):

$$s_{R} = \sqrt{\left(\frac{1}{n_{CO}}\right)^{2} s_{n_{H_{2}}}^{2} + \left(\frac{n_{H_{2}}}{n_{CO}^{2}}\right)^{2} s_{n_{CO}}^{2}}$$

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