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PREFACE

The California Energy Commission’s (CEC) Energy Research and Development Division supports energy research and development programs to spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution and transportation.

In 2012, the Electric Program Investment Charge (EPIC) was established by the California Public Utilities Commission to fund public investments in research to create and advance new energy solutions, foster regional innovation and bring ideas from the lab to the marketplace. The CEC and the state’s three largest investor-owned utilities—Pacific Gas and Electric Company, San Diego Gas & Electric Company and Southern California Edison Company—were selected to administer the EPIC funds and advance novel technologies, tools, and strategies that provide benefits to their electric ratepayers.

The CEC is committed to ensuring public participation in its research and development programs that promote greater reliability, lower costs, and increase safety for the California electric ratepayer and include:

- Providing societal benefits.
- Reducing greenhouse gas emission in the electricity sector at the lowest possible cost.
- Supporting California’s loading order to meet energy needs first with energy efficiency and demand response, next with renewable energy (distributed generation and utility scale), and finally with clean, conventional electricity supply.
- Supporting low-emission vehicles and transportation.
- Providing economic development.
- Using ratepayer funds efficiently.

*Low-Temperature Microplasma-Assisted Hydrogen Production from Biogas for Electricity Generation* is the final report for the low-temperature microplasma-assisted hydrogen production from biogas for electricity generation project (Contract Number EPC-15-082) conducted by the University of California Merced. The information from this project contributes to the Energy Research and Development Division’s EPIC Program.

For more information about the Energy Research and Development Division, please visit the [CEC’s research website](www.energy.ca.gov/research/) or contact the CEC at 916-327-1551.
ABSTRACT

This project explored applying low temperature microplasma to convert biogas (a mixture of methane and carbon dioxide) to hydrogen. Unlike conventional biogas conversion technologies that require fuel-combustion and operate at high temperatures, the process proposed in this project is powered by electricity and conversion is possible at moderate temperatures. This new technology could help California achieve its mandated goals and targets including reduced carbon pollution and greenhouse-gas emissions, and increased development and adoption of renewable resource energy technologies.

The plasma reactor for conversion of methane (CH$_4$) and carbon dioxide (CO$_2$) into hydrogen (H$_2$) and carbon monoxide (CO) was designed and built in-house. The research team tested and evaluated performance for a range of operating conditions. The highest registered conversion rate of CH$_4$ and CO$_2$ to syngas (mixture of H$_2$ and CO) was about 30 percent for the conditions tested in this project. Future conversion rates could be higher with greater interaction times between the gases and the plasma. The researchers designed an analytical model to predict conversion rates for conditions that could not be tested for this project. The model predicts that designing an array of microplasma reactors to work in tandem would improve the performance of the technology.

The successful demonstration of this laboratory-scale plasma reactor makes it a promising technology for further studies with the ultimate goal of commercialization. Long-term benefits of converting biogas to hydrogen and carbon monoxide include a reduction in greenhouse gas emissions through generation of clean fuel from biogas and, in the future, a potential decrease in energy costs for California’s electricity ratepayers.

Keywords: Plasma, biogas, hydrogen, reforming, renewable energy

Please use the following citation for this report:

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EXECUTIVE SUMMARY

Introduction
With growing worldwide concern about climate change and global warming, there is an intensifying emphasis on clean-energy technologies that eliminate or minimize the greenhouse gas emissions that contribute to climate change. Of all of the greenhouse gases, the two major contributors to the greenhouse-gas effect are carbon dioxide and methane. There is, therefore, an urgent need to develop technologies able to convert these potent greenhouse gases into nontoxic, nongreenhouse gases. In particular, conversion of the mixture of carbon dioxide and methane (two major components of biogas) to carbon monoxide and hydrogen (referred to as synthesis gas or syngas) is a promising method that could help to curb greenhouse emissions. This conversion process uses two potent greenhouse gases to produces hydrogen that can be used as a clean fuel for electricity generation and in fuel-cell vehicles or in stationary storage applications. A second product of the conversion process, carbon monoxide, could be used as a precursor for a range of hydrocarbon compounds that are typically produced from fossil fuels. Therefore, a conversion technology that transforms biogas into syngas could ultimately contribute to California’s mandated push toward reducing use of fossil fuels and greenhouse-gas emissions.

On a commercial scale, such a process already exists and is a major source of hydrogen. This process, referred to as steam reforming, converts a mixture of water steam and methane into a mixture of carbon monoxide and hydrogen at high temperature. A disadvantage of this method is that high temperatures are achieved by burning fossil fuels, reducing the benefits of the conversion process. As California moves to reduce the use of natural gas and toward the electrification of various industries, it is important to identify electricity-based alternatives to steam reforming that will convert the rich supply of biogas in California into clean fuel. This processes is particularly crucial today since future electricity generation will be based more on renewable energy resources, which in turn, will ultimately result in cleaner technological processes.

Plasmas – in which gaseous substances, such as methane and carbon dioxide, are broken down to ions – and clean electricity set the foundation for an environmentally attractive technology in a variety of chemical reactions. More importantly, the state of plasma matter is reached at relatively low temperatures. For example, lightning (a naturally occurring discharge) makes nitrogen dioxide, nitric oxide, and other chemicals that otherwise require high temperatures for their formation. As with any emerging technology, commercial readiness proceeds from the conceptual stage, to laboratory scale, to pilot scale, before investors will ultimately consider its commercialization. In spite of the clear promise of plasma-based technologies for driving chemical processes, including conversion of greenhouse gases to hydrogen, this technology’s readiness level is currently low. Therefore, more laboratory-scale studies are required to improve understanding of the process and test its feasibility before this innovative technology’s development can proceed to the next level on its path to commercialization and widespread adoption.
Project Purpose
This applied research and development project studied and evaluated the use of chemically reactive plasmas to electrochemically convert biogas to hydrogen. The research project addressed knowledge gaps in a plasma-facilitated biogas conversion by designing, building, and testing a microplasma-based reactor. The constructed reactor took in a mixture of carbon dioxide and methane at its inlet and converted it to synthesis gas. The research project also evaluated the microplasma reactor by studying its conversion rate under various operating conditions, resulting in the development of a simplified analytical model that can predict reactor performance even under conditions that were not tested. The University of California, Merced team built and tested a microplasma-based reactor for converting greenhouse gases into hydrogen.

Project Approach
The University of California, Merced team designed the microplasma reactor. The chosen configuration included a quartz tube with a steel rod as the inner electrode, and a copper sheet wrapped around the quartz tube as the outer electrode. The rate of gases flowing into the reactor was controlled with flow meters. Gases flowing out of the reactor were analyzed using gas chromatography, which separates, identifies, and quantifies gaseous molecules in a mixture. The laboratory-scale prototype of biogas convertor built by research team was used to study the dependence of conversion rates and efficiency under various operating parameters (such as the residence time) to maximize its performance. The outcomes of these experiments then guided development of a simplified analytical model to design an array of microplasma reactors.

Project Results
The team successfully demonstrated the lab prototype. Key results of the project included the complete design, fabrication, and testing of a microplasma reactor capable of converting a mixture of carbon dioxide and methane to hydrogen and carbon monoxide. For the reactor tested for this project (that is, based on its specific dimensions), the conversion rate from biogas to hydrogen at a flow rate of 20 milliliters of simulated biogas per minute was about 25 percent. For comparison, the conversion rate for a commercialized steam reforming process is in a range between 65-75 percent. The conversion rate of plasma reactor depends on a flow rate and declines with increased flow rates.

Although the demonstration of designed plasma reactor was successful, its performance and energy efficiency require further work and improvement. The University of California, Merced team attributes the demonstration’s lower-than-expected conversion rate and energy efficiency performance to the restricted range of frequencies (between 20 kilohertz [kHz] and 70 kHz) in the power supply unit used to ignite the plasma. Frequencies above 70kHz could, therefore, lead to better conversion and energy efficiencies. All results of this research are replicable, so the setup could be accurately replicated by following the details discussed in this report.

During this project the research team encountered and resolved several technical and non-technical problems. One was pressure buildup in the reactor that could result in detachment of the inlet and outlet flanges from the quartz tube and potentially lead to cracking of the quartz tube. Real-time monitoring of flow rates allowed the team to resolve the issue with the
pressure build-up. Lower flow rate improved performance of the reactor by increasing the residence time, which in return led to a higher conversion rate.

Future research could focus on increasing the excitation frequencies and advancement of reactor set-up. It would improve the performance and move the technology closer to a pilot-scale readiness level.

**Technology/Knowledge Transfer/Market Adoption (Advancing the Research to Market)**

The results of this research are of interest and relevance to fellow researchers in academic institutions world-wide and to industrial partners in the energy sector. This research has been shared in presentations through several invited talks including to Applied Materials Inc., Purdue University, the University of Antwerp (Belgium), and Case Western Reserve University. Project results and conclusions will also be published in a peer-reviewed energy journal. Some results will appear on the Principal Investigator’s research group webpage. This webpage is open to all interested individuals and organizations from any part of the world and will include acknowledgment of its funding. The project and its importance for the state’s energy future have also been introduced to students in the fourth through sixth grades at the Merced City School District’s Science, Technology, Engineering & Arts, Mathematics (STEAM) Center – a program that helps the next generation of engineers and scientists learn about careers in clean energy technologies.

**Benefits to California**

The results from this project could inform future research activities in the field of hydrogen technologies and benefit California’s utility ratepayers in long-run. This research explores the clean use of biogas available in California by converting its greenhouse gas constituents in either syngas for electricity generation, or hydrogen for use in energy storage and fuel-cell-powered vehicles applications. Biogas as a feedstock for hydrogen production offers a sustainable path to production of hydrogen.
CHAPTER 1: Introduction

California’s vast network of energy generation and delivery systems is increasingly affected by extreme weather events. Coastal floods, drought, and wildfires, linked to climate change, adversely affect both the statewide electricity system and the electric grid’s ability to transmit electricity to California’s millions of end-use electric customers. Current predictions also anticipate an increase in the frequency of these extreme weather events (Bedsworth et al.).

Renewable energy technologies significantly reduce or eliminate the greenhouse gas emissions that contribute to climate change. Integration of renewable energy in the state’s energy portfolio is at the heart of California’s mandated efforts to meet its ambitious energy and clean-air targets. While solar and wind farms are important renewable options, their intermittency is inherently limiting. Fuel cell technology, which creates a chemical reaction between hydrogen and oxygen, can reliably generate clean electricity at any time of the day, in any season. One of the limiting factors holding back wider application of fuel cells is availability of the hydrogen that fuels them. Despite its natural abundance, hydrogen is seldom available in a form that can directly be used as fuel to produce energy. This project’s research and proposed recommendations address how best to overcome this hurdle.

The primary goals of this research project were to design, build, and effectively operate a pilot-scale, non-thermal plasma reactor capable of converting biogas to synthesis gas—which is a mixture of carbon monoxide and hydrogen. Specific objectives included: building a microplasma reactor ignited by using high-voltage nanosecond pulses; determining the role of various plasma operating parameters on reactor performance; and, finally, applying that data to scale-up design and demonstration of an array of microplasma reactors. Using plasma makes this process electricity-driven instead of heat-driven (as in steam reforming). Use of plasmas are inherently more efficient. Because an electricity-driven process requires no combustion to generate heat, no fossil fuels are burned, and no greenhouse gasses are produced.
CHAPTER 2:  
Project Approach

Low-temperature plasma is a broad research area with various possible operating schemes. This project uses an atmospheric-pressure microplasma (not to be confused with a low-pressure plasma) that operates within a quartz-tube reactor. Specifically, this type of plasma is a dielectric barrier discharge plasma, made up of an inner electrode that is coaxial with the cylindrical quartz tube and an outer electrode that is wrapped around the quartz tube. The quartz tube contains stainless steel flanges at both inlet and exit. The stainless-steel flanges were designed and fabricated at University of California (UC) Merced’s machine shop. O-rings were used to seal the interface of the quartz tube with the flanges to ensure there was no leakage. The inlet flange was equipped with a hole that holds the inner electrode in place. The inlet flange was also equipped with two inlet ports for the gas flows processed by the microplasma reactor. Figure 1 shows the individual components of the reactor.

![Figure 1: CAD Drawing of Plasma Reactor](source: UC Merced)

A high-voltage sinusoidal excitation is applied at the inner steel electrode, while the outer electrode is grounded. The project uses an off-the-shelf power supply (PVM500 from Information Unlimited) that fits the project requirements. The power supply was capable of producing peak voltages up to 20 kilovolts (peak-to-peak 40 kilovolts) and allowed frequencies of between 20 kHz and 70 kHz. This high-voltage excitation energized the electrons and led to ionization of the gas molecules flowing through the quartz tube. The set-up allowed for modification of various reactor geometrical parameters including the length of the outer copper electrode (wrapped around the quartz tube) (Figure 2), and quartz tube diameter (which would require changing the end flanges and the O-rings). The setup does not currently include a mechanism to measure the temperature of the electrodes during operation though a moderate temperature increase is anticipated. Appropriate safety measures are in place in the lab for handling and operating high-voltage equipment. The inlet gas (in the current case this is either carbon dioxide, methane, or a mixture of both) flows through 1/16-inch stainless tubes (purchased from Shimadzu Inc.). The diameter of the tubing is based on the inlet ports in the stainless-steel flange that is attached to the quartz tube. The gas sources are standard cylinders purchased from Praxair Inc., with the purity of both carbon dioxide and methane greater than 99 percent. The flow rates for each of the gases is adjusted using a Sierra mass flow controller with flow rates adjustable between 0 and 5 standard liters per minute. A methane purifier (Figure 2) was also installed between the methane cylinder and the mass
flow controller, with a separate moisture trap installed between the carbon dioxide gas cylinder and the mass flow controller. Gases entering the quartz tube, flow through the reactor and undergo the plasma-assisted conversion process. It should be noted that there is no external heating required for this set-up because the conversion chemistry is triggered and driven by the energetic electrons in the dielectric barrier discharge plasma. The energy of electrons (and hence the conversion dynamics) can be controlled by modifying the geometrical parameters of the reactor as well as the excitation (peak voltage and frequency). The exit flange was equipped with one outlet port through which the gases produced by the reactor (along with the unconverted inlet gases) flowed to the gas chromatograph, where it was characterized. The same kind of stainless tubing connects the outlet to the injection ports in the gas chromatograph.

**Figure 2: Laboratory Setup**

An image of the laboratory setup showing the footprint of the reactor and the power supply along with other components such as a flow controllers.

Source: UC Merced

The setup constructed as part of the current project uses a custom GC-2014 gas chromatograph from Shimadzu Inc. The gas chromatograph is equipped with a thermal conductivity detector and a flame ionization detector. The gas chromatograph is connected to a computer dedicated to post-processing and provides results of the analysis performed by the gas chromatograph. A photo of the gas chromatograph is shown in Figure 3. The operation of the gas chromatograph requires the use of hydrogen and helium gases, which are directly supplied through the injection ports from cylinders purchased from Praxair Inc. In spite of the high degree of purity of the gases in these cylinders, additional gas purifiers were included, as mandated by the manufacturers of the gas chromatograph (Shimadzu Inc.).
The Shimadzu gas chromatograph equipment for analysis of outlet gases from the plasma reactor.

Source: UC Merced

As part of this project’s setup phase, a suction exhaust system to handle the gases used and produced during this project was also installed. Previously, the lab studied argon microplasmas that did not require an exhaust control. For this project, however, an exhaust system was designed and installed, which caused minor delays. The exhaust system design was performed by engineers at the UC Merced School of Engineering, with installation performed by outside contractors. An image of the exhaust system is shown in Figure 4.

Figure 4: Snorkel Exhaust

The snorkel exhaust installed in the lab to fulfill safety requirements, such as removal of carbon monoxide (toxic) from the air.

Source: UC Merced
At first, the microplasma reactor setup was tested for plasma ignition. Figure 5 shows the pink glow indicating the plasma in operation.

**Figure 5: Plasma Reactor**

The plasma shown with argon as the working gas. Argon creates a plasma with a pink emission.

Source: UC Merced
CHAPTER 3:  
Project Results

With the ultimate goal of converting a biogas prototype (a mixture of carbon dioxide and methane) to a synthesis gas (a mixture of carbon monoxide and hydrogen) using a novel and energy-efficient approach with non-thermal plasma, the project began with independent testing of each of these gases. Specifically, either methane or carbon dioxide flowed into the inlet. Though the reactor was equipped with two inlets to allow gas flows from two different sources, one of the inlets was not used in the experiments described here. The mass-flow controllers located upstream of the reactor inlet allowed a specified flow rate of either carbon dioxide or methane. It should be noted that the mass flow controllers were specific to the gases they were calibrated for. Because two different gases were used, two independent mass flow controllers were required.

Once a gas-flow rate was set, the microplasma was turned on (microplasma shown in Figure 6) to initiate the conversion process.

Figure 6: Plasma Reactor at Different Light Exposures

Plasma reactor in action (at two different light exposure levels). The plasma resembles a glow.

Source: UC Merced

The product composition was analyzed using a Shimadzu GC-2014 gas chromatograph described earlier in progress reports and in the microplasma construction report previously submitted to the Energy Commission. For all performed experiments, a peak voltage of about 9 kilovolts at a frequency of around 25 kHz was used. While this voltage is very high, the current levels at which the microplasma operates are quite low, resulting in a power input measured in watts. The gas chromatograph requires only a small volume (approximately 5 ml) of exhaust gas for sampling. Hence, the microplasma reactor is turned off once the gas chromatograph valve shuts off, indicating that exhaust is no longer being fed into the analysis chamber of the gas chromatograph. A typical gas chromatograph is composed of a spectrum-like plot where each peak corresponds to a certain species of molecule and the total concentration of a given species can be obtained by integrating the area under the spectrum curve. All experiments were performed using both the thermal conductivity detector and the flame ionization detector that are parts of the gas chromatograph. The thermal conductivity
detector detects hydrogen, nitrogen, and oxygen; and the flame ionization detector detects methane, carbon dioxide, and other C₂ species (with two carbon atoms). A typical gas chromatograph output uses the characteristic retention times of each species to determine their concentration. Example plots are shown in Figure 7. The detectors used to obtain the plots are indicated in the top right corner. The peak (in the thermal conductivity detector) at 2.5 minutes (min) corresponds to hydrogen with the peak at 3.6 minutes, indicating oxygen (possibly from ambient air). The peak at 5 minutes corresponds to nitrogen (also from ambient air).

**Figure 7: Sample Output from Thermal Conductivity Detector**

A sample output from the thermal conductivity detector (TCD1) of the gas chromatograph showing presence of gases in the mixture at various residence times.

Source: UC Merced

For the methane gas input, experiments varied the flow rate from 0.125 L/min to 2 L/min. The outer electrode width was set to 1.5 inches to correspond to the length of the reactor. The dependence of flow rate on reactor performance (specifically conversion percentage) is through variations in residence times. If a certain amount of methane gas is stagnant and treated by the plasma for a long period of time (5 min), it is bound to demonstrate significant conversion through broken bonds. The duration of flowing gas exposure to the microplasma also depends on the gas flow rate as well as the reactor length (or outer electrode width). It was observed that the outflow (after microplasma treatment) was still predominantly methane, although hydrogen concentrations increased rapidly with decreasing flow rate, which directly correlates with previously stated residence-time results.
A sample output from the Flame Ionization Detector of the gas chromatograph showing presence of gases in the mixture at various residence times. The peaks detected include methane (6.6 min), CO2 (8.2 min), and C2 species (10.4 min).

Source: UC Merced

Additionally, in experiments where the electrode width was increased to 3 inches, the hydrogen concentrations grew significantly for a given flow rate (compared to an electrode width of 1.5 inches). The electrode width was somewhat limited by the length of the quartz tube used and is something that can be easily modified in future experiments. Other parameters that will be varied in the future include the diameter of the quartz tube, which is limited by the dimensions of the inlet and outlet flanges. Modifying these elements will require machining suitable flanges at UC Merced’s machine shop and will be performed in future. One other design parameter that is of relevance is the peak voltage that has been maintained as a constant in all experiments performed so far. The experiments performed for carbon dioxide demonstrated a similar trend where increasing amounts carbon monoxide were detected when the flow rate was decreased, or the electrode width increased.

While a qualitative description of the dependence of various parameters has been discussed, the reactor performance still needs to be quantified with specific emphasis on the conversion percentage, as well as the conversion efficiency. During this phase of the project, the microplasma reactor constructed as part of an earlier phase was used to perform measurements of conversion of methane and carbon dioxide. Though quantitative results are yet to be presented, the conversion was observed to increase with decreasing flow rate as well as increasing electrode width. Future work will present quantitative results for each of the configurations discussed here and will present an optimized set of geometrical and operating parameters for the microplasma reactor.

The microplasma reactor set-up described earlier was used to perform all experiments contained in this report. While previous reports only reported preliminary results that demonstrated the feasibility of making measurements, this report provides quantitative
information on the actual performance of the reactor. Experiments were performed for the plasma-assisted conversion of pure methane, pure carbon dioxide, and a mixture of equal parts of methane and carbon dioxide. The conversion process involved flowing gas through the microplasma reactor designed and built for this project. The microplasma reactor was comprised of a quartz tube with an inner stainless-steel electrode (powered) and an outer copper electrode (ground).

One of the design modifications implemented during this period was inclusion of a cylindrical-end connection (machined at UC Merced) to the inner electrode that allowed changes to the discharge gap (defined as the gap between the quartz tube and the inner electrode). Figure 8 shows the end connection that decreases the discharge gap when compared with the set-up used in previous reports. Note that the end connection is attached to the existing electrode and, therefore, allows adjustment of the discharge gap without modifying the inlet and outlet flanges which were designed and machined specifically for the thin electrode. The plasma was ignited using a high voltage (approximately 10 kilovolts) sinusoidal excitation at a frequency of about 30 kHz. The products flowing out of the reactor were analyzed using a Shimadzu 2014 gas chromatograph described previously in this report. The length of the outer electrode can vary, which in turn increases the residence time and the plasma’s interaction with the gas. The residence time can also be increased by decreasing the flow rate of the gas(es) flowing through the reactor. All experimental data reported here are based on three to five samples. While there were some outliers in many of the datasets, at least three reproducible runs supported the project’s reported data.

**Figure 9: Electrode Attachment**

The electrode attachment that enables the easy change of discharge gaps.

Source: UC Merced

The first set of experiments was performed for pure methane flowing through the reactor. The microplasma reactor helps break the bonds of methane (leading to the formation of various hydrocarbons, including ethane and ethylene) apart from hydrogen, which is the desired product of this process. The gas chromatograph measures concentrations of hydrogen, $C_2s$ (including various species with two carbon atoms) apart from methane itself. There are two performance parameters—conversion rate and selectivity—that require quantification for any conversion process. The conversion rate is the amount of methane converted to other
components. The methane consumed is not all converted into hydrogen. The fraction of methane that is converted to hydrogen is referred to as the selectivity of hydrogen. Since hydrogen is the desired product, the goal is to achieve as high of a hydrogen selectivity as possible. The product of conversion rate and selectivity gives the yield. To obtain a good yield for a given species, high conversion rates and selectivity are optimum. High selectivity combined with a poor conversion rate or vice versa is not desirable. For example, a conversion rate of 50 percent combined with a hydrogen selectivity of 80 percent results in a yield of 40 percent ($0.50 \times 0.80 = 0.40$). In other words, 40 percent of the initial methane that flows through the reactor is converted to hydrogen gas.

**Figure 10: Conversion and Selectivity of Hydrogen for Plasma-Assisted Conversion of Methane at Various Flow Rates**

![Graph showing conversion rate and selectivity vs. flow rate](image)

Source: UC Merced

Figure 10 shows the conversion rate and selectivity for methane conversion to hydrogen. The other species (approximately 30 percent selectivity) formed during this conversion include hydrocarbons with two or more carbon atoms (C2). Individual hydrocarbons formed are not distinguished in the context of this work. Under project’s testing conditions, the electrode length was set at approximately 7.5 centimeters (cm) with a fixed-voltage amplitude. Therefore, the residence time was determined by the flow rate. As the flow rate increases, the conversion rate decreases while the hydrogen selectivity remains about the same. Therefore, increasing flow rate leads to an overall decrease in the yield of hydrogen. One of the encouraging results is that most of the methane is converted primarily to hydrogen and very little amount of C2 hydrocarbons is produced.

One of the parameters, that wasn’t investigated within the constraints of this project was the influence of voltage used to produce the plasma on the efficiency of the process. This could be explored in the future.
The second batch of experiments was performed for pure carbon dioxide instead of methane as the flowing gas; all other parameters remained the same. The primary conversion products for pure carbon dioxide flowing through the reactor included carbon monoxide and oxygen, with carbon monoxide as the targeted end product.

The next set of experiments was performed for an equal mixture of methane and carbon dioxide flowing through the reactor for conversion to carbon monoxide and hydrogen. Unlike the separate conversion of methane and carbon dioxide, these experiments were complicated due to possible side reactions happening in the plasma reactor and leading to formation of non-targeted hydrocarbons. Figure 11 shows the conversion rate and selectivity of carbon monoxide for various flow rates and residence times. The conversion rate is very similar to that for methane only, with a maximum conversion rate just under 25 percent. The process was restricted by the current flow meter (Sierra Instruments). It was not possible to lower flow rates, which could have potentially increase the conversion rate. An easier approach to increase residence time would be to increase the length of the electrode, which will be performed in future work. The selectivity for carbon monoxide was about 64 percent, with 33 percent for oxygen. While this does not total 100 percent, this was attributed to measurement errors.

Figure 11: Conversion and Carbon Monoxide Selectivity for Plasma-Assisted Conversion of Carbon Dioxide as a Function of Flow Rate

All experiments performed for an equal mixture (50/50 mixture) of methane and carbon dioxide showed slightly higher conversion rates of about 32 percent, than the those reported for pure methane or pure carbon dioxide. The selectivity remained constant at about 70 percent, while the conversion rate decreased with an increasing flow rate. While these datasets need more investigation (with experiments performed for various other methane to carbon dioxide ratios), one of the possible explanations is that the reactive radicals (high
energy particles) generated in plasma from due to splitting of start reagents (carbon dioxide and methane) have promoting effect on gas conversion.

Looking ahead, several research questions need to be answered, including an energy-efficiency quantification. Specifically, the current setup does not allow the measurement of power which, in turn, affects the ability to make critical energy-efficiency predictions. An immediate upcoming task is to add capacitors to the setup that can quantify power using the Q-U Lissajous method. Other future research opportunities include experiments conducted for various mixture ratios of methane and carbon dioxide to further improve both conversion rates and selectivity.

The two plots that represent key outcomes of the single microplasma reactor tested during previous phases appear in Figure 10 and Figure 11. Specifically, the figures show the conversion rates of methane to hydrogen and carbon dioxide to carbon monoxide achieved using the microplasma reactor designed, fabricated and tested as part of the current project. These results were used to calculate design parameters for an array of microplasma reactors operating in tandem. Based on the observations gathered during the experiments it was noticed that reactor’s selectivity does not depend on the gas mixture flow rate, while its efficiency demonstrates a much stronger dependence on the flow rate and, thusly, the residence time. For calculations of the residence time for gases flowing through the plasma reactor, the following steps were undertaken: 1) Flow rate in ml/min was converted into m³/s.

Cross sectional area of reactor was calculated based on the diameter of the outer quartz tube (0.25 cm) and diameter of the inner electrode (0.19 cm). The calculated cross-sectional area is 2.0735E-4 square meters (m²).

The residence time was calculated from the mean velocity of gas flow (0.00161 meters per second (m/s) and the electrode length of 0.075 m and equals to 46.6 s.

Assuming reactor’s conversion rate is 25 percent, 20 ml of methane/carbon dioxide mixture will produce 5 ml/min of hydrogen, which can then be connected in parallel, with other reactor to make a tandem. An array of reactors could increase the yield of hydrogen linearly. For this project, the footprint of an array of ten reactors was estimated based on the dimensions of a single reactor. Figure 12 shows a schematic array of 25 single reactors where the inner electrode is shown in brown and the annular plasma shown in purple. The estimated length was based on the electrode length, with a correction to account for the reactor’s additional fittings. A reasonable estimate for the total length of the array of reactors was 15 cm (twice the electrode length). Therefore, a 22.5 cm x 22.5 cm x 15 cm reactor theoretically could produce 0.125 L of hydrogen from 0.2 L mixture of methane and carbon dioxide per minute. This system could be useful for production of onboard hydrogen in limited quantities since pre-filled hydrogen tanks would be unnecessary. While fuel-cell-powered cars are clearly one area where this technology could be used, the technology could also potentially be extended to medium-scale hydrogen production systems for residential sector.
It should be noted that the hydrogen production rate discussed here is based on operating at the maximum possible conversion rate. Operating at higher flow rates may lead to higher yields at the expense of lower conversion rates. For example, the need for a temporary surge in hydrogen production could be met by increasing the flow rate. Operating at 50 ml/min would produce 7.5 ml/min of hydrogen per reactor (based on a 15 percent conversion rate) that would correspond to 187.5 ml/min of hydrogen. Of course, this would consume more of the feedstock gas (per unit yield of hydrogen) and is comparable to traditional engines that produce higher power at lower efficiencies. While hydrogen is the byproduct of interest in this research, other byproducts of splitting methane (or a mixture of methane and carbon dioxide, would include higher hydrocarbons, such as ethylene, acetylene, and carbon monoxide. Therefore, an important component of this system would be a separation of the gaseous products. While there are several potential strategies to separate the products to retrieve pure hydrogen one challenge would be the size of these systems.

While the described array design is based on simple scale-up of the exact reactor that was tested in this research project, it would be important in future studies to formulate compact models that could be used to modify the electrode length; this would permit significantly different reactor lengths and, therefore, residence times. In this context, a theoretical model was formulated, where $dx$ is a section of length in the microplasma reactor.
Therefore, the local conversion factor per unit length is $\alpha$ (units of 1/m) and the fraction of
feedstock gas converted to hydrogen is $\alpha \cdot dx$. Integrating over a finite length, one gets an
exponential relation between the incoming flow rate of methane and outflow rate of hydrogen
(which is the same as the conversion rate):

$$Conversion\ rate = (1 - e^{\alpha L \cdot q})$$

where $q$ represents the flow rate and $L$ represents the electrode length. A similar expression
can be obtained by defining a conversion parameter per unit time $\eta$ (with units of 1/s)
expressed here, where $T$ is the residence time of the system.

$$Conversion\ Rate = (1 - e^{\eta T})$$

As expected, equations involving the electrode length and residence time are related,
confirming the linear relationship between $\alpha$ and $\eta$. It is worth noting that an infinite electrode
length (or an infinite residence time) will ensure that all methane is converted to hydrogen.

The exponential relation between total conversion rate and residence time is also evident from
results shown earlier in Figure 10 and Figure 11. The conversion rate for a given residence
time can, therefore, be computed based on the residence time and the value of $\eta$ (depending
upon the discharge gap). Another aspect of this process is its energy requirements and
Corresponding implications. The microplasma reactor tested in the lab used about 5 watts of
power (estimated based on the Lissajous method). Using an array of microplasma reactors
would result in a linear power increase as a function of the number of reactors included in the
array. A 25-array reactor would, therefore, consume 125 watts to produce hydrogen at a rate
of 187.5 ml/min. Assuming standard temperature and pressure conditions, 1 mole of hydrogen
occupies 22.4 L, so 187.5 ml/min is equivalent to 0.0084 mol/min. One mole of hydrogen
combines with one mole of oxygen to provide approximately 285,000 joules of energy.
Therefore, the 0.0084 moles of hydrogen will combine with the corresponding stoichiometric
quantity of oxygen to produce about 2,000 joules of energy (assuming 85 percent efficiency
for the fuel cell). This is equivalent to about 33 watts of power from the fuel cell. The other
method of producing hydrogen is electrolysis. Here about 5 KWh are required to produce 1 m$^3$
of hydrogen. Hence, production of 187.5 ml of hydrogen per minute corresponds to about 56 W for electrolysis and is about 10 times less efficient than plasma reactor-based technology. However, it is worth noting that the feedstock for the tested plasma reactor-based technique
and the electrolysis technique are different with the latter using water for conversion to hydrogen and oxygen. The focus of this current project is to produce hydrogen from biogas.

Steam reforming, fueled by fossil energy, is yet another commercialized technology for
hydrogen production, and while it is currently more efficient than the proposed plasma-fueled
process, but has a high carbon footprint that negates advantages of using hydrogen as energy storage medium.
CHAPTER 4: Technology/Knowledge/Market Transfer Activities

The UC Merced team performed various activities in order to transfer the knowledge gained from this research project. These activities can be broadly classified into dissemination of results in conferences and peer-reviewed journal articles as well as in talks at academic institutions and industrial organizations. Specifically, certain aspects of the results were presented in the APS Division of Plasma Physics conference held in San Jose. Preliminary results generated during the project became a part of a Master’s thesis. Others results from this project will be part of a PhD thesis. The UC Merced team is currently working on preparation of a manuscript to be submitted to a peer-reviewed journal. This manuscript will include project results in their entirety and describe both the setup and the model developed. While neither the theses nor the journal article are available for free (and require subscription), the pre-print version of the manuscript will be made available on the Principal Investigator’s website as well as websites such as the Research gate, for wider dissemination of the results.

During this project, the principal investigator was also invited to several academic institutions including Purdue University, Applied Materials, and the University of Antwerp. The principal investigator ensured that the talks delivered and discussions held during these meetings included information about the current project. The Principal Investigator is also involved in activities with the local school district and has contributed as a guest speaker to the local STEAM center. During these visits, the Principal Investigator has described the results obtained as part of this project. As the project technology readiness level increases in the near future (where the principal investigator plans to continue the tasks even after the project is completed), the principal investigator plans to engage potential industry partners and investors interested in the commercialization of the product.
CHAPTER 5: Conclusions and Recommendations

This research project designed, fabricated, tested, and analyzed a low-temperature plasma-based approach for converting biogas (methane and carbon dioxide) to syngas (carbon monoxide and hydrogen). The advantage of using a plasma-based system is that the reactions that enable the splitting of methane and carbon dioxide for eventual conversion to carbon monoxide and hydrogen are driven by electrons, so they require much lower temperatures than traditional steam-reforming. The plasma reactor was designed by the principal investigator’s group and consisted of a quartz tube with a coaxial inner electrode and an outer electrode wrapped around the quartz tube. The plasma reactor demonstrated the ability to split methane and carbon dioxide into hydrogen and carbon monoxide with conversion percentages (ratio of hydrogen to methane or carbon monoxide to carbon dioxide) that increased with higher residence times. The residence time, defined as the time of interaction between the plasma and the inlet gases, increased along with increased electrode area and decreased with flow rate. The maximum conversion percentage achieved for the laboratory-scale reactor was about 30 percent. While this may seem low, this percentage was specific to residence times that corresponded to the reactor’s geometry that was tested. Based on this experimental data, an analytic model was designed that proposed an exponential relation between residence times and conversion percentages. While the overall project was successful, the performance of the reactor could be improved by operating at higher frequencies than those used in this project. Another other way to increase conversion is by testing an array of reactors, though this approach would require larger reactors. Once performance is improved, this promising concept could be scaled up to pilot-scale before moving, ultimately, into commercialization.
CHAPTER 6: Benefits to Ratepayers

Generation of renewable hydrogen from biogas benefits Californians in several ways. A key environmental benefit is reduction of greenhouse gas emissions. Two potent greenhouse gases (carbon dioxide and methane) that contribute to climate change are consumed to produce hydrogen, an element expected to play a significant role in satisfying California’s ambitious clean-air targets through 2050. With the fast-growing energy storage and zero emissions vehicles market, a corresponding increase in hydrogen demand is expected. Another benefit is that the biogas as a feedstock for hydrogen production is widely available throughout the state. Since this technology is still in its infancy, its exact cost and benefits have not yet been detailed, though this research indicates that energy costs would be reduced with this emerging technology’s broad application. Finally, the adoption of this new technology could lead to the creation of well-paying technical jobs.
## LIST OF ACRONYMS

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<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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REFERENCES


