Investigation of Atmospheric Pressure Plasma Source for CO_2 Dissociation

Laura Spencer, A. D. Gallimore

University of Michigan, Ann Arbor, MI, United States

Abstract: This work experimentally investigates the dissociation of CO_2 in an atmospheric pressure surface-wave discharge. A 2-kW microwave power supply is used to sustain the plasma contained in 1-cm-diameter quartz tube. Optical emission spectroscopy is recorded at varying axial positions along the quartz discharge tube to give evidence of the different species present. Diagnostics taken with a residual gas analyzer are used to monitor the evolution of atomic and molecular species in the system, revealing CO and oxygen as the main products of the plasma-chemical reactions. For plasma-assisted CO_2 dissociation to be a practical and cost-effective solution for the climate change challenges, the process must meet certain standards of efficiency. Therefore the energy efficiency and conversion efficiency of the plasma system is examined for CO_2 dissociation.

1. Introduction

The continual and increasing use of fossil fuels throughout the world has advanced concerns of atmospheric carbon dioxide (CO_2) concentrations, causing a swell of scientific interest to ease the predicted effects of global warming. One possible solution to decrease atmospheric concentrations of CO_2 is the use of a plasma source to break apart the molecule into carbon monoxide (CO) and oxygen. The CO can be filtered out for use in the chemical industry, or CO can be further combined in the plasma system with other gases such as hydrogen or water vapor to produce usable hydrocarbons.

The design and use of a surface wave discharge excited by microwaves is experimentally examined here for the purpose of CO_2 dissociation. The discharge is operated at atmospheric pressure, and is sustained by a 2.45-GHz, 2-kW microwave supply. This plasma source was chosen for its ability to create a nonequilibrium plasma [1,2], which is essential for exciting the vibrational modes of CO_2 that results in the most efficient dissociation process [3]. Energy efficiency and conversion efficiency are examined using data taken from a residual gas analyzer (RGA) to ultimately determine the practical utility of this system for large-scale industrial use for the dissociation of CO_2. Thus far, the highest energy efficiency achieved in this system is ~20%, while the highest conversion efficiency (yield) achieved is ~100%. Optical emission spectroscopy is also used qualitatively for species identification.

2. Experimental Setup

The microwave plasma source, Fig. 1, consists of a 2.45-GHz magnetron head powered by a 2-kW power supply. A three-port circulator with dummy load attaches to the magnetron head to prevent reflected power from damaging the magnetron. A directional coupler placed next to the circulator is used for forward power and reflected power measurements. Next to the directional coupler, a three-stub tuner is used to match the plasma, which is created and sustained by the *Surfaguide* device [4,5,6,7]. The magnetron head, the circulator, dummy load, and the *Surfaguide* are all water cooled to prevent any thermal damage.

The *Surfaguide* consists of a standard rectangular waveguide with a reduced height section that the discharge tube pierces perpendicularly through the wide waveguide wall. This reduced height section of waveguide provides a maximum electric field at the location the microwaves cross the discharge

tube, enabling for a highly efficient plasma source. Extending above and below the *Surfaguide* are two bronze cylindrical waveguides, 33 cm in length, which encase the discharge tube to prevent the emission of microwave radiation. In order to visualize the plasma and use emission spectroscopy diagnostics, 5-mm-diameter holes spaced 3.8 cm apart were placed axially along one face of each cylindrical waveguide. The discharge tube is a 10-mm-ID quartz tube 107 cm in length, surrounded by a larger 38-mm-ID quartz cooling jacket 66 cm in length through which a cooling fluid flows to prevent melting of the quartz discharge tube. The cooling fluid, polydimethylsiloxane, was chosen for its low microwave absorption, low viscosity, and high optical transmission [8,9]. The fluid passes through a recirculating chiller with heat exchanger, Polyscience Model 6860T, to keep the fluid at a desired temperature.
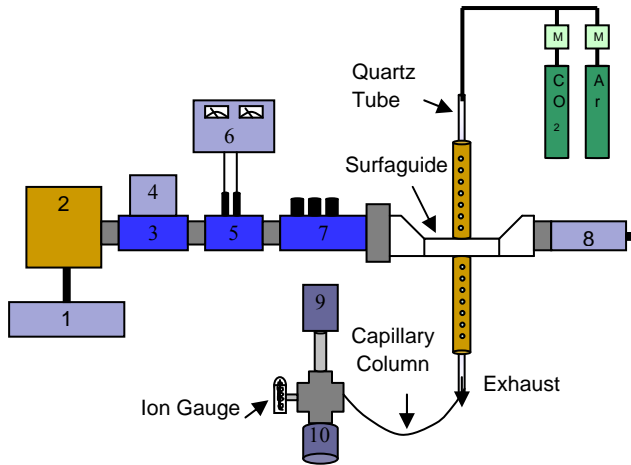

Figure 1. *Microwave plasma setup. 1) 2-kW power supply, 2) Magnetron head, 3) Three-port circulator, 4) Dummy load, 5) Directional coupler, 6) Power meters, 7) Three-stub tuner, 8) Sliding short circuit, 9) RGA, 10) Turbo pump.*

3. Diagnostics

A) Mass Spectrometry

A Stanford Research Systems RGA100 residual gas analyzer is used in all experiments to identify the species present in the system. The maximum allowable operating pressure of the RGA is 10^{-4} torr, which is much lower than the plasma discharge operating regime of atmospheric pressure. To accommodate the pressure requirements of the RGA, a separate chamber evacuated by a Varian V70LP turbomolecular pump was used to house the RGA, reaching a base pressure of 10^{-9} torr. Also attached to the chamber was an ion gauge for pressure measurement and a 0.102-mm-ID fused silica capillary column 4 m in length. One end of the capillary column is at atmospheric pressure and is inserted into the exhaust end of the discharge tube for plasma species measurement. The other end of the column is attached to the RGA chamber. The length and ID of this capillary is able to maintain a pressure of 6×10^{-5} torr inside the RGA chamber, while remaining open to atmosphere at one end.

In order to extract quantitative information from RGA spectra, a calibration must be performed for each gas species to be identified in the plasma. The RGA was calibrated using the method described by Nguyen [10] in which a known fixed amount of argon flows into the plasma chamber with a varying amount of the target gas species (e.g. CO) to be identified. A calibration factor can be determined from the ratios of the partial pressure of Ar and the target gas and from the known flow rates of each gas. Once the calibration factor is found, a flow rate of the species created in the plasma discharge can be calculated from Eq. 1.

$$\dot{m}_i = \frac{\dot{m}_{Ar}}{CF} \frac{P_i}{P_{Ar}} \qquad (1)$$

In Eq. 1, $\dot{m}_i$ is the plasma produced flow rate of the species in question, $\dot{m}_{Ar}$ is the constant flow rate of Ar, CF is the calibration factor, P_i is the partial pressure of the target species in question, while P_{Ar} is the partial pressure of Ar. The ratio of partial pressures can be plotted vs. the ratio of flow rates for CO_2, CO, and O_2 and a linear relationship should be found. The slope of the line represents CF.

B) Error Analysis

For all RGA data presented here, results shown are the mean values of a sample of measurements. Error bars represent one standard deviation among the spread in the measurement sample, which includes error from flow control instrument measurements. The sample size for the calibration data is four sets with three spectra for each data point. The sample

size for the CO_2 plasma species measurements is two sets of data with three spectra for each data point.

C) Optical Emission Spectroscopy

The Ocean Optics HR4000 spectrometer is used to take optical emission data in the visible region from 400 – 800 nm with an optical resolution of 0.22 nm at FWHM. Currently the optical emission spectrum can only give information on the radiative species in the visible region. With the installation of a more defined grating providing increased resolution, the optical emission data can be used in conjunction with SpecAir to gain information on the rotation and vibrational plasma temperatures.

4. Results and Discussion

In this experiment only two parameters were varied: the ratio of CO_2:Ar and the microwave power. The flow rate of CO_2 ranged from 1 to 8 slm, while the flow rate of Ar was kept at a constant of 6 or 8 slm. The power ranged from 1 to 2 kW. First the plasma was ignited using a tesla coil with only Ar flowing through the discharge tube. Then CO_2 was slowly added in small increments to keep the reflected power below 10 W until the desired CO_2 flow rate was reached.

A) Optical Emission Species

To sustain the discharge with the addition of high amounts of CO_2 (>100 sccm), the power must remain at 1000 W or greater.   Below this threshold, the plasma extinguishes from lack of electrons. As CO_2 is introduced into the discharge the energy switches to vibrational excitation of CO_2 rather than ionization. Since Ar is easily ionized, it is used as the background gas to supply electrons. This effect is experimentally observed in the emission spectrum shown in Figure 2.   Both spectra have been normalized to the largest intensity of the pure Ar spectrum.   The red solid line represents the 1-kW pure Ar discharge with a flow rate of 6 slm and with forward microwave power. The strong Ar neutral lines are the dominant species present in the spectrum.   The blue dotted line represents the spectrum after 1 slm of CO_2 is added to the discharge at 1.5 kW of forward microwave power.

All of the Ar neutral lines disappear and the dominant spectral lines are the C_2 Swan Band System showing band heads at (0,0), (1,0), and (0,1), 516, 473, 562 nm respectively [11]. A weaker O I line is present at 777 nm as well as O II around 425 nm. A small amount of the N I line near 744 nm is also evident.

The absence of the Ar neutral lines indicates that most of the Ar is becoming ionized and serving as the main electron production mechanism.   The presence of the C_2 Swan Band system indicates that carbon is being generated either from CO_2 or CO. It is unlikely that the reaction $CO_2 \rightarrow C(s) + O_2$ is responsible because of the high energy required, ΔH=11.5 eV/mol. However the reaction $CO + CO \rightarrow CO_2 + C$ requires only 5.5 eV/mol with $E_a = 6$ eV and leads to the formation of C atoms in the gas phase free to combine with other carbon atoms to form C_2. This reaction is accelerated by vibrational and electronic excitation of CO molecules, which is easily stimulated in nonequilibrium plasmas [3]. The intensity of the C_2 band is relatively weak due to the rapid reverse reaction $C + CO_2 \rightarrow CO + CO$ with $E_a = 0.5$ eV.   There are no CO_2 bands in the spectrum because CO_2 is transparent in the visible region and under these operating conditions the majority of CO_2 is converted to CO [11].
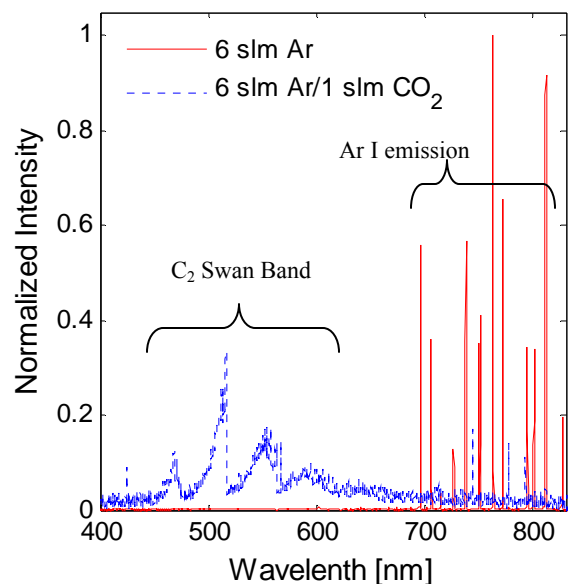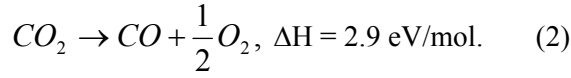

Figure 2. *Optical emission spectrum for a pure Ar discharge at 6 slm and 1 kW of microwave power (solid red), and 6:1 slm Ar:CO$_2$ discharge at 1.5 kW (blue dotted).*

B) Energy and Conversion Efficiency

The total enthalpy of CO_2 decomposition can be represented by

$$CO_2 \rightarrow CO + \frac{1}{2}O_2, \; \Delta H = 2.9 \text{ eV/mol.} \qquad (2)$$

From (2) CO and O_2 are expected to be the main products of dissociation in the plasma system. Thus, the energy efficiency can be examined by determining the amount of CO produced in the system using mass spectrometry data. Eq. 1 defines the relationship between the partial pressure measurements taken by the RGA and the flow rate of species leaving the system, which is used to calculate the production of CO.

The energy efficiency is defined as

$$\eta = \frac{\Delta H}{E_{CO}} = \alpha \cdot \frac{\Delta H}{E_v} = \dot{m}_{COout} \cdot \frac{2.9}{power}. \qquad (3)$$

As explained in [3,12], ΔH is the dissociation enthalpy and E_{CO} is the actual energy cost to create one CO molecule in the plasma system. E_{CO} can be defined as the ratio of specific energy input, E_v (given by the ratio of microwave power to CO_2 flow rate into the system), to conversion efficiency, α. The conversion efficiency is defined as

$$\alpha = \frac{\dot{m}_{COout}}{\dot{m}_{CO_2in}} \qquad (4)$$

The energy efficiency is plotted in Figure 3 for varying flow rates of CO_2 from 1 to 8 slm for operating condition of 6 slm Ar and 8 slm Ar. The highest energy efficiency achieved under these operating conditions is around 20%. The conversion efficiency is plotted is Figure 4 with maximum conversion reaching about 100%. In both plots the solid markers represent a background gas of 8 slm Ar, and the unfilled markers represent a background gas of 6 slm Ar.

The data trends in Figures 3 and 4 suggest that energy efficiency is inversely proportional to conversion efficiency. These trends are consistent with what was found using a low pressure rf plasma source in [12]. The highest energy efficiency of around 20% occurs for the lowest specific energy of

about 4 eV/mol with 8 slm of CO_2 flowing in the discharge. Yet this operating condition has the lowest conversion efficiency of about 25%. Likewise, the operating condition with highest conversion efficiency of about 100% at $E_v = 27$ eV/mol has the lowest energy efficiency of 10%. As the flow rate of CO_2 increases with the power remaining constant, fewer molecules will be vibrationally excited resulting in a lower conversion rate for low values of specific energy. Both efficiencies are higher for almost all operating conditions when the background is 8 slm Ar versus 6 slm Ar. Since Ar is the main supplier of electrons in the system, as discussed previously, the conditions with a higher flow rate of Ar can produce more electrons leading to higher conversions of CO_2 to CO.

As discussed in [12], an energy efficiency greater than 50% must be achieved for this technology to be of practical use when a fossil fuel such as natural gas provides the energy source. At a level of $\eta < 50\%$, the plasma system begins to create more CO_2 molecules than it can destroy due to the energy required for the chemical reactions to take place. A better option is to use alternative "clean" energy sources to power the CO_2 reduction system. However the yield of CO molecules tends to drop with high values of η. This problem can be solved by installing a recirculating system that separates out the unconverted CO_2 molecules to be passed through the plasma system until they are converted to CO and O_2.

5. Conclusion

The efficiency of CO_2 dissociation in an atmospheric pressure microwave plasma discharge has been experimentally examined. The highest energy efficiency for the conversion of CO_2 to CO achieved thus far in this system is 20% corresponding to a conversion efficiency of 25%. Given the trends in the data, it is expected that higher flow rates of CO_2 will produce higher values for energy efficiency, though the conversion efficiency may suffer. To address this issue, catalyst material will be injected into the discharge to increase the rate of conversion of CO_2 to CO, while maintaining energy efficiency.
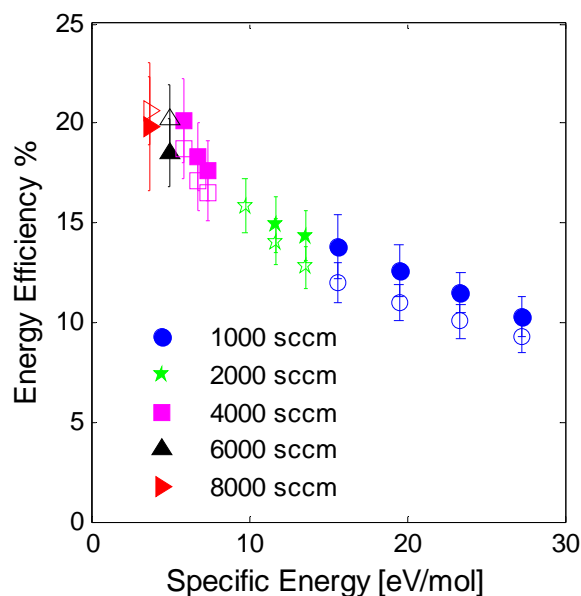
Figure 3. *Energy efficiency for the conversion of CO$_2$ to CO. Solid markers for 8 slm Ar background and unfilled markers for 6 slm Ar background.*
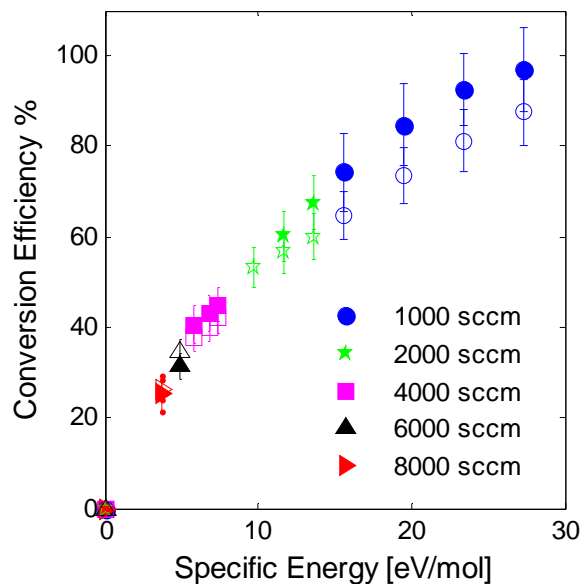

Figure 4. *Conversion efficiency of CO$_2$ to CO. Solid markers for 8 slm Ar background and unfilled markers for 6 slm Ar background.*

Acknowledgements

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