DISSOCIATION OF CO_2 IN A RADIO-FREQUENCY PLASMA SOURCE

L. SPENCER[%], A. D. GALLIMORE[#] AND S.V.T. NGUYEN[&]

Department of Aerospace Engineering, Plasmadynamics and Electric Propulsion Laboratory, University of Michigan ,Beal Ave 1320,48109 Ann Arbor, United States, e-mail:laspen@umich.edu

Current dependence on fossil fuels to satisfy increasing energy needs has created an overabundance of CO_2 emissions. This project aims to use a radio frequency (rf) plasma source to dissociate CO_2 completely into solid carbon and gaseous oxygen to reduce CO_2 concentrations in the atmosphere. An rf plasma excited by a double helix antenna with an axial magnetic field is used to create the CO_2 discharge. This paper presents an analysis of the species present in the CO_2 plasma based on data taken from a residual gas analyzer. The main products of the CO_2 dissociation were found to be CO and O_2. Future work will involve using an atmospheric pressure glow discharge for practical real world application to dissociate CO_2.

Key words: carbon dioxide, rf plasma

1 Introduction

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The need to align economic desires, environmental desires, and energy needs is a significant challenge facing the United States and the world today. The U.S. currently produces the majority of its energy from fossil fuels. The combustion of these fossil fuels creates carbon dioxide as a by-product, making it a leading cause of climate change

One way to address the climate change challenge is to combine both reduction of CO_2 emission and removal of CO_2 in the atmosphere. This paper experimentally investigates a method for reducing levels of CO_2 in the atmosphere via an rf plasma source. The main dissociation mechanism is electron impact collisions. Electron densities in rf plasmas can range from 10^{16} to 10^{19} m^{-3} depending on which operating mode is used (capacitive, inductive or helicon). Given the high densities of helicon plasmas, it is suspected that a helicon plasma could be the most efficient for CO_2 dissociation. For this reason, an rf plasma source was used in this experiment, however the plasma never reached helicon mode due to the operating conditions. Helicon mode is typically reached at pressures ~ 1 mtorr – 20 mtorr with rf power greater than 1000 W [1]. The operating pressures for this experiment ranged from 50 mtorr – 270 mtorr and rf power never exceeded 1000 W.

2 Experimental Setup

A. Facilities and Plasma Source

A cylindrical vacuum chamber measuring 2.4 m long and 0.6 m in diameter was used for all experiments presented here. The plasma source is mounted on the side of the chamber on a port measuring 14.5 cm in diameter. The vacuum chamber is evacuated by a dry scroll pump capable of reaching a base pressure of ~2 mtorr. For operation in high vacuum, a CVI M500 cryopump is also attached to the chamber to achieve a base pressure of ~1 x 10^{-7} torr. A 15-cm-diameter by 40-cm-long quartz tube used for gas inlet is vacuum sealed to the side of the chamber by a rubber O-ring. A double helix antenna is wrapped

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[%] Graduate Student – Ph.D. Candidate, Applied Physics Program
[#] Arthur F. Thurnau Professor, Laboratory Director
[&] Graduate Student – Ph.D. Candidate, Aerospace Engineering

around the tube which is connected to a 13.56-MHz, 3-kW rf power supply through a pi-style matching network. The matching network reduces the reflected power to about 10 W or less during operation. Three separate magnetic coils surround both the antenna and tube. A Lambda DC power supply capable of outputting a maximum of 60 A supplies current to the magnetic coils. The peak magnetic field strength along plasma source centerline is 415 G.

B. Residual Gas Analyzer

Mass spectroscopy measurements are taken with a SRS RGA100 residual gas analyzer. Because the vacuum chamber pressure during source operation is higher than the operating pressure ceiling of the RGA (10^{-4} torr), the RGA is attached to a small differentially-pumped subchamber that is connected to the top of the vacuum chamber (Fig. 1). This arrangement allows for experimental operating pressures in the main vacuum chamber to be higher than 10^{-4} torr while the RGA subchamber pressure is kept well below this threshold.

A variable leak valve isolates the RGA chamber from the plasma chamber. A Varian V70LP turbomolecular pump is attached directly to the RGA chamber which can achieve a base pressure of 10^{-8} torr. Inside the RGA, gas species are ionized and identified according to the mass/charge ratio. The collected ion current is sent to the RGA software that converts current to partial pressure by the equation $I = S*p$, where I is the ion current in A, p is the partial pressure in torr, and S is the gas sensitivity factor [2]. Figure 1 shows a diagram of the vacuum chamber, plasma source, and RGA chamber.
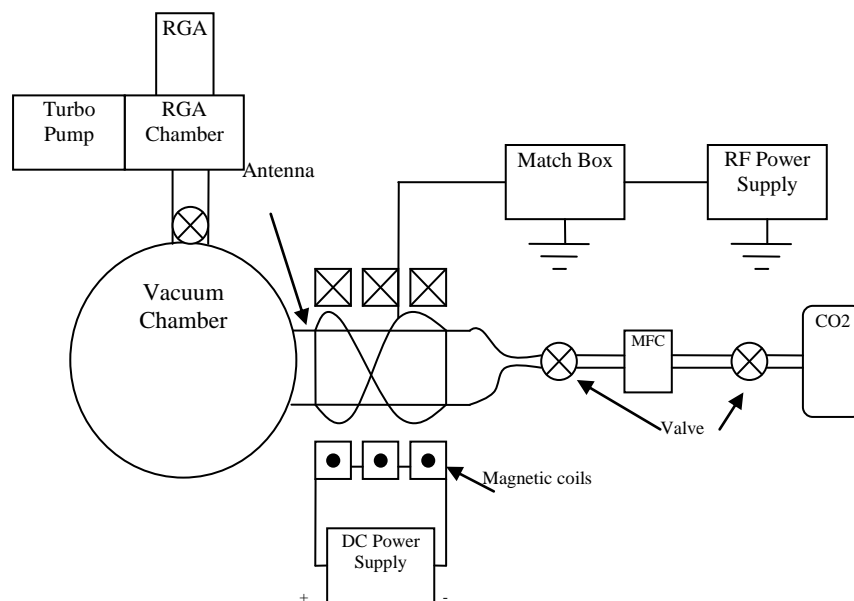

Figure 1 : Experimental setup.

3 Results and Discussion

A. Species Identification

Based on data taken from the RGA, the main species present in the CO_2 plasma were CO_2, CO, and O_2 with mass/charge ratios of 44, 28, and 32 respectively. Given that the atomic masses of CO and N_2 are 28.0101 and 28.0134 respectively, the RGA is not capable of distinguishing between singly-ionized CO and singly-ionized N_2. To eliminate this ambiguity, a preliminary background scan was taken before any CO_2 flowed into the

chamber. Assuming that there are no significant leaks in the vacuum system, the partial pressure of N_2 should not increase with the introduction of CO_2. By subtracting the background scan from all subsequential scans, any resulting partial pressure measurements at the mass/charge ratio of 28 can be taken to correspond to singly-ionized CO.

To insure that the RGA data accurately represent the species present in the vacuum chamber, gas correction factors for CO_2, CO, and O_2 must be used. The ion current is converted to a partial pressure by using the gas sensitivity of N_2. Ideally, gas sensitivity factors for CO_2, CO, and O_2 should be found experimentally for the specific vacuum facility and operation conditions used here. The sensitivty factor for the specific gas can then be used to calculate the partial pressure at the specified mass/charge ratio. However, first a simple approach was used to analyze RGA data by assuming the following gas correction factors for CO_2, CO, and O_2 relative to N_2: 1.45, 1.05, 1.01, respectively [3]. These factors were derived from electron impact ionization cross sections and were used to correct the sensitivity factor in calculating partial pressure. Future work will involve directly calculating the gas sensitivity to increase the level of accuracy.

B. Effects of Mass Flow Rate, RF Power, and Magnetic Field

To determine the optimal conditions for CO_2 dissociation, three parameters were varied : mass flow rate of CO_2, rf power, and magnetic field strength. The data presented here are for 10, 25, 50, and 100 sccm CO_2, which correspond to operating pressures of 50, 100, 167, and 270 mtorr, respectively. RF power was set to 250, 500, 750, and 1000 W, and the applied dc current for the magnetic coils was set to 0, 25, and 50 A for each flow rate. Figures 2(a)-(d) display the normalized gas partial pressure with respect to the RGA chamber pressure for CO_2, CO, and O_2 plotted versus rf power.

The general trend shown in the plots below is that the partial pressure of CO increases with increasing power for each flow rate. Likewise, the partial pressure of CO_2 decreases with increasing power, indicating the dissociation of CO_2. The partial pressure of O_2 remains relatively constant for plots (a) – (d). Figure 1(a) shows the lowest partial pressure of CO_2 and the highest partial pressure of CO. As mass flow rate is increased, the partial pressure of CO_2 becomes higher while the amount of CO produced becomes slightly lower. This result is expected because as more gas molecules are introduced into the system at a fixed power, the collision rate increases making it less likely that an electron will have enough energy to dissociate a molecule of CO_2. An analysis of magnetic field strength indicates no significant trend in plots (a) – (d), suggesting it does not affect dissociation; however data is inconclusive at this time.

The main dissociation reactions of CO_2 via electron impact are as follows:

$$CO_2 + e^- \rightarrow CO_2{}^* + e^-$$
$$CO_2{}^* + e^- \rightarrow CO + {}^1\!/_2 O_2$$
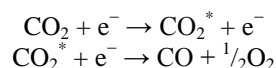
Therefore, it was expected that the partial pressure of CO and O_2 would increase [4]. However, O_2 concentrations remain constant, suggesting that the oxygen molecules are reacting with other species present in the system like hydrogen or carbon. It is unlikely that CO further dissociated into C and O, due to its continual increase in partial pressure with increasing power. If CO were to dissociate, one would expect a decrease in partial pressure and an increase in the partial pressure of oxygen, neither of which were observed here. The bond dissociation energy of CO is twice the bond dissociation energy of CO_2 (11 eV vs 5.5 eV), making it significantly harder to break the CO bonds, thus explaining why CO dissociation did not occur here [5].
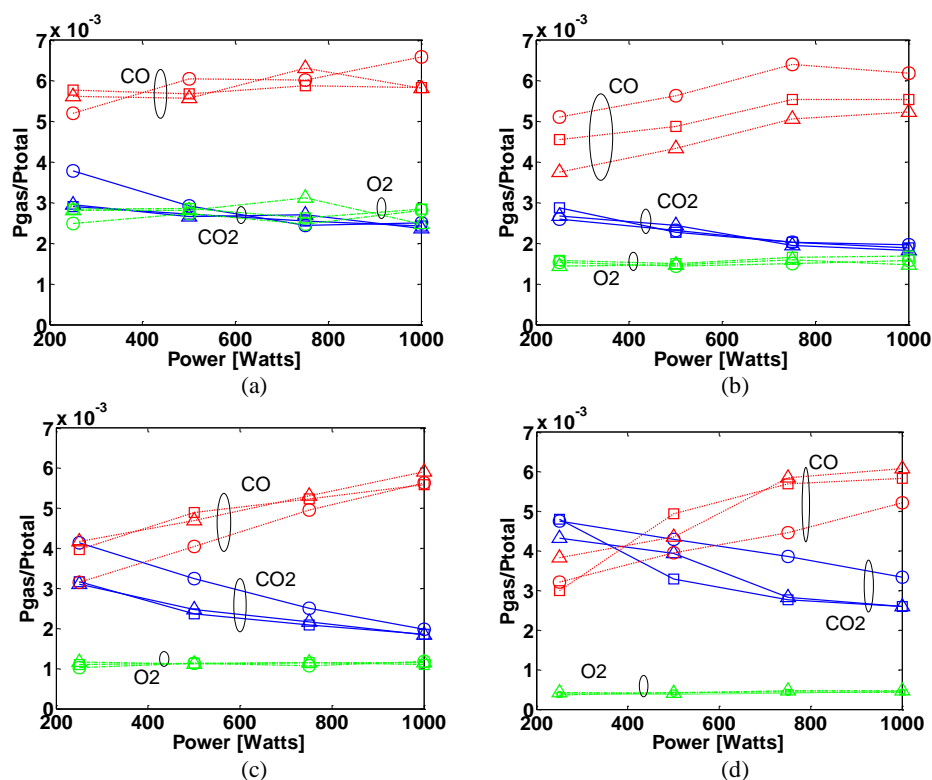
Figure 2: Ratio of CO_2, CO, O_2 partial pressure to total RGA chamber pressure for (a) 10 sccm, (b) 25 sccm, (c) 50 sccm, and (d) 100 sccm. Applied dc current to magnetic coils 0 A (circle), 25 A (square), and 50 A (triangle).

4 Conclusions

The work presented here has shown the successful dissociation of CO_2 via an rf plasma source. The optimal operating conditions that decreased CO_2 partial pressure the most proved to be the lowest flow rate of 10 sccm CO_2 with the highest rf power of 1000 Watts. Magnetic field variations showed no significant effect and yielded inconclusive results. Further dissociation of CO was unsuccessful given restraints of operating conditions. This was expected given the high bond dissociation energy of CO. The future construction and operation of an atmospheric pressure glow discharge will determine the practical capabilities of CO_2 dissociation to mitigate global warming.

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