Conversion of CO₂ in a gliding arc discharge reactor: Discharge characteristics and the effects of different parameters

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Abstract—In this work, a knife-shaped gliding arc discharge (GAD) reactor driven by a modulated pulse power supply was used to convert CO₂. The discharge image, voltage and current waveforms of GAD were recorded experimentally. The effects of gas flow rate, input voltage, and the duty cycle of power supply on CO₂ conversion were studied. A CO₂ conversion of 3.8% and energy efficiency of 39.6% could be achieved. Compared with other non-thermal plasmas, GAD has a slightly lower CO₂ conversion but higher energy efficiency. In addition, the capacity of CO₂ treated by GAD (6 L/min) was significantly higher than other non-thermal plasmas (e.g. 25 mL/min-125 mL/min in corona discharge and dielectric barrier discharge).

1. Introduction
In recent years, the emission of greenhouse gases and the search for sustainable energy sources have attracted considerable attention. CO₂ is a well-known source of greenhouse gases that contributes to climate change [1], and the increasing concentration of CO₂ has a serious impact on the health of the ecosystem. From this perspective, it is crucial to reduce CO₂ emissions. Converting CO₂ into valuable fuels or chemicals is consistent with the idea of sustainable development. The direct decomposition of CO₂ into CO (eq.1) has attracted the interest of scholars.

\[ \text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2 \quad \Delta H = 280 \text{kJ/mol} \quad (1) \]

Non-thermal plasma technology (NTP) can effectively convert CO₂ into valuable fuels and chemicals, so it is a promising solution. The high-energy electrons produced by non-thermal plasma have extremely high electron temperature (1-10 eV), which can effectively activate the inert molecules (e.g. CO₂) and produce active species (such as excited atoms, ions, molecules, and free radicals) to participate in chemical reactions. The gas kinetic temperature of non-thermal plasmas can be as low as room temperature [2], which means most of the energy is used for chemical reactions. In addition, the flexibility of non-thermal plasma systems (instant switch on and off) allows the reaction system to utilize intermittent renewable energy sources (such as wind and solar). This can solve the imbalance between energy production and consumption and create a carbon neutral-network [3-4]. Currently, a variety of non-thermal plasma systems have been used to directly dissociate CO₂, such as dielectric barrier discharge(DBD) [5-6], microwave discharge [7-8], GAD [9-10]. It is well known that the most effective way to directly dissociate CO₂ into CO is the vibration excitation of CO₂ [11]. In DBD discharge system, the conversion of CO₂ is mainly achieved by electron collision excitation, and the
vibration excitation of CO₂ has little effect on the conversion of CO₂, so the energy efficiency of the conversion is usually less than 10%. In microwave discharge, CO₂ can be effectively dissociated by vibration excitation of CO₂, but the discharge system must be kept at low pressure (50-200 torr), which is undoubtedly undesirable from the perspective of industrial application.

GAD can be easily characterized by the existence of the flame between the electrodes. The flame is generated by the rapid movement of the arc between the electrodes under the action of gas flow. Compared with other non-thermal plasmas, the GAD has higher electron energy and energy density, which can reach a non-equilibrium state at atmospheric pressure and achieve effective CO₂ dissociation through vibration excitation. Therefore, GAD is one of the most promising plasmas in CO₂ conversion. To our knowledge, there are few reports on the direct conversion of CO₂ by GAD generated by the modulated pulse power supply.

In this work, a knife-shaped gliding arc reactor driven by a modulated pulse power supply was used for CO₂ conversion. Discharge image and discharge waveforms were recorded to better understand the development of the gliding arc. The effects of gas flow rate, input voltage, and duty cycle of power supply on CO₂ conversion, energy efficiency, CO selectivity, CO yield were studied.

2. Experiment

In this experiment, a knife-shaped gliding arc reactor was used, and the arrangement of the experimental system was shown in Fig. 1. The reactor consists of a Teflon bracket, a quartz cover, and a pair of stainless steel knife-shaped electrodes. The electrodes were symmetrically distributed on both sides of the nozzle, and the shortest gap between them was 3 mm. The gas feedstock used in the experiment was pure CO₂ (99.999%), and its flow rate was controlled by a mass flowmeter (6-10 L/min). The gas entered through the nozzle in the central of the base and flowed out through the center outlet at the bottom of the quartz cover. One of the electrodes was grounded and the other was connected to a high-voltage modulated pulse power supply (Nanjing Suman Electronics Corp CTP-2000K). The pulse signal of the modulated pulse power supply consists of a sine wave with a fixed frequency of 5 kHz. The amplitude, frequency, and duty cycle of the pulse can be adjusted. The voltage and current signals were measured by the 1000:1 Tek P6015A high voltage probe and Tek P6021 current probe, respectively. A four-channel TDS2014C oscilloscope with a 200 MHz bandwidth and a 2.0 GS/s sampling rate recorded the voltage and current signals. The image of the arc during the discharge was recorded by a Panasonic digital camera. Gases were analyzed by a gas chromatograph (Shanghai Tianmei Corp. GC7900). In order to evaluate the CO₂ conversion performance, the CO₂ conversion, energy efficiency, CO yield, and CO selectivity were calculated experimentally. The calculation formulas are as follows:

\[
X(\text{CO}_2)(\%) = \frac{\text{CO}_2\text{converted(mol/min)}}{\text{CO}_2\text{introduced(mol/min)}} \times 100\% \tag{2}
\]

\[
Y(\text{CO})(\%) = \frac{\text{CO}\text{produced(mol/min)}}{\text{CO}_2\text{introduced(mol/min)}} \times 100\% \tag{3}
\]

\[
S(\text{CO})(\%) = \frac{\text{CO}\text{produced(mol/min)}}{\text{CO}_2\text{converted(mol/min)}} \times 100\% \tag{4}
\]

\[
\eta(\%) = \frac{\text{CO}_2\text{feed flow rate (mol/min)} \times X(\text{CO}_2)(\%) \times \Delta H(\text{kJ/mol})}{\text{Discharge power(W)} \times 60/1000} \tag{5}
\]

As shown in eq. (5), \( \Delta H \) is 280 kJ/mol for pure CO₂ splitting process, and the discharge power was calculated as the product of discharge voltage and current.
3. Results and Discussions

3.1. Typical discharge characteristics of GAD

In the process of GAD, the arc length, and the arc position changed rapidly, and this change intuitively reflected in voltage, current and macroscopic motion features. This section helps to understand the basic discharge characteristics of the GAD by recording voltage, current and discharge images.

The GAD was carried out in the atmosphere of pure CO₂. The input voltage was 8 kV and the duty cycle was 80%. As shown in Fig. 2(c), the arc moved downward gradually under the push of CO₂ gas, and a stable two-dimensional plasma region appeared between the electrodes from a macroscopic perspective. Fig. 2(a) recorded the voltage and current waveforms within 100 ms in the discharge process. When the pulse signal arrived, the voltage reached 10 kV instantly and a current of about 25 A was generated at the same time, and then the voltage peak and current peak rapidly dropped. The air gap between the electrodes was broken down and the arc connected the shortest gap between the electrodes. Under the action of the gas, the arc gradually extended downward, while the voltage peak gradually increased. When the power supply was unable to sustain the energy loss of the long arc, the arc disappeared and reignited at the shortest gap between the electrodes, which was called a gliding period. Fig. 2(b) recorded the discharge waveform for the first 2 ms in a gliding period. The breakdown voltage and the maintained voltage gradually increased during the GAD process, and a discharge cycle was about 0.2 ms. Thus, hundreds of breakdowns occurred during a gliding period as the arc moved down the electrode.
3.2. CO₂ conversion performance in GAD

3.2.1 Effect of gas flow rate
The GAD is formed under the push of gas flow, which significantly affects the CO₂ conversion performance. In this section, input voltage was fixed at 8 kV, the duty cycle of the power supply was 60%, and the gas flow rate varied from 4 L/min to 10 L/min. As shown in Fig. 3(a), the gas flow rate increased from 4 L/min to 6 L/min, and the CO₂ conversion gradually increased from 2.88% to 3.13%. When the flow rate exceeded 6 L/min, the CO₂ conversion gradually decreased and finally reached 1.78%. The energy efficiency also showed a similar trend, reaching the maximum value of 61.13% when the gas flow rate was 6 L/min. It was worth mentioning that CO₂ conversion and energy efficiency increased gradually when the gas flow rate was lower than 6 L/min. Previous studies (such as corona discharge [12] and dielectric barrier discharge [6]) showed that under the condition of fixed input voltage, the increase of gas flow rate would accelerate the speed of CO₂ molecules passing through the plasma region, so the CO₂ conversion gradually decreased. In addition, in the process of using plasma to decompose CO₂, there is a reciprocal relationship between CO₂ conversion and energy efficiency, and the increase of CO₂ conversion is usually accompanied by a decrease in energy efficiency. However, appropriately increasing the gas flow rate of CO₂ (4 L/min-6 L/min) would push the arc to glide a longer distance along the electrode and formed a larger plasma region in GAD. With the increase of discharge intensity (discharge power from 42 W to 64 W), more CO₂ molecules were converted, so the CO₂ conversion and energy efficiency were improved. Fig. 3(b) showed CO selectivity and CO generation at different gas flow rates. The CO generation was slightly lower than the CO₂ conversion, and the CO selectivity was about 95%. The results showed that CO is the main carbon-containing product in the process of CO₂ dissociation. There was no carbon deposition on the electrodes, and the missing carbon molecules may be related to the uncertainty of instrumental measurements. Therefore, in the following sections, the selectivity and yield of gas products are no
longer concerned, and the CO₂ conversion and energy efficiency are taken as the main indicators to evaluate the conversion performance. According to the experimental results, a CO₂ flow rate of 6 L/min was recommended to obtain a relatively high CO₂ conversion (3.13%) and energy efficiency (61.13%) in the GAD system.

![Fig. 3 Effect of gas flow rate on CO₂ conversion: (a) CO₂ conversion and energy efficiency; (b) CO yield and selectivity.](image)

3.2.2 Effect of input voltage

Fig. 4 showed the CO₂ conversion performance under different input voltages. In the process of increasing the input voltage from 7 kV to 10 kV, the CO₂ conversion increased from 2.9% to 3.48%. However, the energy efficiency showed a decreasing trend, reaching a maximum of 66% when the input voltage was 7 kV, and dropping to 51% when the input voltage was 10 kV. With the increase of the input voltage, the discharge power of GAD increased (54.8 W to 85 W), and the electric field intensity, high energy electron density, and active particle density in the plasma region also increased. When CO₂ molecules passed through the discharge region, the probability of being bombarded by high-energy electrons was increased, and more CO₂ molecules were dissociated into CO. As the input voltage increased from 7 kV to 10 kV, the energy efficiency dropped sharply. This may be because more energy is dissipated in the air due to the extension and elongation of the arc, and a large amount of energy is not used for CO₂ conversion, so the conversion efficiency gradually decreased. The possible reason was that the arc extension and elongation led to more energy dissipation in the air, and a large amount of energy was not used for CO₂ conversion, so the energy efficiency gradually decreased. The results showed that the energy efficiency decreased to 51% with the increase of input voltage, but the CO₂ conversion increased to 3.48%.

![Fig. 4 Effect of input voltage on CO₂ conversion](image)
3.2.3 Effect of duty cycle

The feature of the modulated pulse power supply is that the duty cycle of the pulse can be changed. In this experiment, the carrier frequency is fixed at 5 kHz, the pulse frequency is fixed at 50 Hz, and the pulse period is 20 ms. When the duty cycle is 20%, the single pulse power supply time is only 4 ms, which means that the energy of the modulated pulse power supply to the GAD system is more concentrated, but the reduction of the single pulse power supply time will inevitably lead to lower discharge power. As shown in Fig. 5, when the duty cycle was 20%, the discharge power was only 20 W and the CO₂ conversion was only 1.4%, but energy efficiency was as high as 87.5%. When the duty cycle increased from 20% to 80%, and the discharge power increased from 20 W to 120 W, the CO₂ conversion increased to 3.8%, but the energy efficiency decreased to 39.6%. The increased duty cycle made the discharge power increased rapidly, so the CO₂ conversion would increase. But the energy injected into the system by the power source was more dispersed, and more of it was dissipated as heat, so the energy efficiency gradually decreased. Although the low duty cycle had high energy efficiency, its low CO₂ conversion was not suitable for industrial applications. In summary, when the duty cycle of the power supply was fixed at 80%, the CO₂ conversion and energy efficiency could reach 3.8% and 39.6%, respectively. At this time, GAD was more suitable for CO₂ conversion.

4. Conclusion

In this work, a GAD generated by a modulated pulse power supply was used to convert CO₂. Because the discharge cycle was much smaller than the gliding period, hundreds of electrical breakdowns occurred between the knife-shaped electrodes in a gliding period. The effects of gas flow rate, input voltage, and duty cycle on CO₂ conversion performance were studied. The CO₂ conversion and energy efficiency increased with the increase of gas flow rate, reaching a peak when the gas flow rate was 6 L/min, and then decreased significantly when the gas flow rate further increased to 10 L/min. The main gas product in the CO₂ conversion process was CO, and the missing C molecule may be related to the uncertainty of measurement. The increase of the input voltage and the duty cycle increased the CO₂ conversion, but the energy efficiency decreased accordingly. Based on the experimental results, high CO₂ conversion (3.8%) and energy efficiency (39.6%) could be obtained in GAD system when the gas flow rate was 6 L/min, the input voltage was 10 kV and the duty cycle was 80%. Compared to other typical non-thermal plasmas used for CO₂ conversions, such as corona discharge (CO₂ conversion of 3-20%, energy efficiency less than 10%) [12] and dielectric barrier discharge (CO₂ conversion of 3-33%, energy efficiency less than 10%) [6], the CO₂ conversion of GAD was slightly lower, but its energy efficiency was very high. In addition, the treatment capacity of GAD (6 L/min) was two orders of magnitude higher than corona discharge and dielectric barrier discharge (20-120 mL/min), which was beneficial for industrial applications.
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References
[1] Shah J J, Singh H B. Distribution of volatile organic chemicals in outdoor and indoor air[J]. Environmental Science and Technology, 1988, 22(12):1381-1388.
[2] Tu X, Whitehead J C. Plasma-catalytic dry reforming of methane in an atmospheric dielectric barrier discharge: Understanding the synergistic effect at low temperature[J]. Applied Catalysis B Environmental, 2012, 125: none.
[3] Snoeckx R, Ozkan A, Reniers F, et al. The Quest for Value - Added Products from Carbon Dioxide and Water in a Dielectric Barrier Discharge: A Chemical Kinetics Study[J]. ChemSusChem, 2017.
[4] Mei D, Tu X. Conversion of CO2 in a cylindrical dielectric barrier discharge reactor: Effects of plasma processing parameters and reactor design[J]. Journal of CO2 Utilization, 2017, 19:68–78.
[5] Aerts R, Somers W, Bogaerts A. Carbon Dioxide Splitting in a Dielectric Barrier Discharge Plasma: A Combined Experimental and Computational Study[J]. ChemSusChem, 2015, 8(4):702-716.
[6] Paulussen S, Verheyde B, Tu X, et al. Conversion of carbon dioxide to value-added chemicals in atmospheric pressure dielectric barrier discharges[J]. Plasma Sources Science Technology, 2010, 19(3):34015-34016.
[7] Rooij G, Bekerom D, Harder N D, et al. Taming microwave plasma to beat thermodynamics in CO2 dissociation[J]. Faraday Discussions, 2015, 183.
[8] Thomas, Godfroid, Tiago, et al. Optical characterization of a microwave pulsed discharge used for dissociation of CO_2[J]. Plasma Sources Science & Technology, 2014.
[9] Tu X, Sun, et al. CO2 conversion in a gliding arc plasma: Performance improvement based on chemical reaction modeling[J]. Journal of Co2 Utilization, 2017.
[10] Fridman A, Nester S, Kennedy L A, et al. Gliding arc gas discharge[J]. 1998, 25(2):211-231.
[11] Fridman A. Plasma Chemistry[J]. plasma chemistry, 2008.
[12] Xu W, Li M W, Xu G H, et al. Decomposition of CO2 Using DC Corona Discharge at Atmospheric Pressure[J]. Japanese Journal of Applied Physics, 2004, 43(12):8310-8311.