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Effect of Coaxial Dielectric Barrier Discharge Reactor Configuration on CO_2 Decomposition

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Abstract

For four decades the dielectric barrier discharges (DBDs) has been well-known non-thermal plasma discharges for various applications in science and environment concern such as ozone synthesis, gas decomposition and conversion, air pollution control, excimer laser, material and film surface modifications etc. Thus, the main objective of this present work was to study effect of reactor electrodes configuration on CO_2 decomposition. The quartz coaxial tube was designed as DBD plasma reactor for decomposition of gas. The outer electrode and inner electrode was made of thin flat copper sheet and stainless-steel rod, respectively. The electrical discharge gap between both of electrodes was fixed at 0.5 mm. The argon plasma discharge was generated by a high AC voltage (0-8 kV) with fixed frequency of 7.8 kHz. The inlet mixed gas ratio, discharge gap, applied voltage, outer electrode length, step of gas discharges and inlet gas flow rate was varied in each operating condition. The results showed that percentages of CO_2 conversion relatively decreased with increase of mixing ratio of CO_2:Ar and inlet mixing gas flow rate. In controversy, percentage increase of CO_2 conversion significantly related to high voltage supply. Furthermore, the high percentage of CO_2 conversion (47.2%) has been obtained at 1.3 mm electrical discharge gap.

Keywords: Gas conversions; DBD reactor; Pollution control; Greenhouse gases (GHG)

Introduction

CO_2 is a part of greenhouse gases and has been attracting to the global warming on the earth. It can be more emitted from the transportations, burning and the use of all fossil fuels. The chemical bond of CO_2 is very strong and cannot be dissociate in using of chemical reaction. To dissociate the OC=O double bond, the high temperature has to use at least 1,500°C for thermolysis process and high pressure has been employed to break CO_2. However, this dissociation results are quite low performance comparing to its investment. Even there are many methods to convert CO_2 such as photo-catalytic and photochemical processes, Biochemical processes and Physical processes but it seems to be insufficient process to huge amount of CO_2 conversion in the short period. The most effective process should be easy and encourage us to work on conversion of CO_2. The non-thermal plasma processes have been studied and adopted to avoid those low perform incidences such as glow discharge, corona discharge, dielectric barrier discharge (DBD), radio frequency (RF) discharge and microwave discharge etc. [1-9]. In addition, Indarto *et al.* [1] have been reported the review article about greenhouse gas and toxic gas decompositions through the plasma technologies. In summary, they suggested that the advantage process should be the combined or new alternative process and methods. DBD plasmas had been promoted for a long time for surface modifications, gas treatment, synthesis, etc. The characteristic of DBDs system can initiated plasma and gas reactions using low energy consumption and low temperature at near atmospheric pressure. Even this system is low temperature plasma discharge but electron particles still have high energy enough (ranging of 1-100 eV) to dissociate and breakdown the chemical bond of gas molecules directly [1, 3, 15-19] and modify surface of poly styrene (PS), poly methyl methacrylate (PMMA) and 1:1 mixture of PS:PMMA films in atmosphere [20-23]. The CO_2 conversion using DBD reactor was operated under various conditions such as gas flow rate, gas temperature, power frequency and power input [24]. In addition, some previous work suggested and represented that noble gas containing in gas feeding or placing a solid catalyst in plasma zone can raise the rate of the gas conversion and product yield [1, 4, 6, 12] and it also produced carbon nanotube on the catalyst surface. Furthermore, Tao *et al.* [25] has reported the reviewed article for the opportunity of CH_4-CO_2 reforming in different methods and they suggested that to improve high performance in plasma process for reforming gas there were three factors which were comprised of reactor configuration, electron density and plasma temperature. Recently, Weizong *et al.* [26] reported a gliding arc plasma could convert CO_2 into CO and O_2. a self-consistent two-dimensional (2D) gliding arc model was developed. Their calculated values of the electron number density in the plasma showed reasonable agreement with the experiments.

Thus the main objective of this research was to study effect of physical parameters on CO_2 decomposition via AC high voltage with high frequency applied. The experiments were carried on under the conditions of 4 different mixing gas ratio of carbon dioxide and argon, various applied voltage between 4 and 8 kV, 3 discharge gap interval and 2 electrode configurations. And finally, the suitable operating condition and effect of those parameter on CO_2 decomposition were discussed and presented.

Materials and methods

Theory

The reaction of plasma chemistry for CO_2 decomposition can be shown in Eq.(1) and Eq. (2), after the process of CO_2 decomposition, this CO_2 is converted into CO and O_2 [10-12]. Eq. (1) and Eq. (2) had confirmed that CO and O_2 are the main product, where ΔH is the enthalpy of the reaction. However, O_2 can formed by the recombination of O radicals, and similarly CO_2 also has reformed by the recombination of CO with O radicals and C with O_2 [1, 13]. CO gas product was utilized for hydrocarbon fuel synthesis (e.g. methanol, ethanol and acetic acid synthesis) and for the mineral and metal industries (e.g. smelting and refining processing).

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

$$\mathrm{CO_2} \rightarrow \mathrm{CO} + \mathrm{O}, \Delta\mathrm{H} = 5.5\ \mathrm{eV/mol} \qquad (2)$$

On the one hand, it can be considered in the unit of Joule [14].by following equation below

$$\mathrm{CO_2} \rightarrow \mathrm{CO} + \mathrm{O}, \Delta\mathrm{H} = 529.8\ \mathrm{kJ/mol} \qquad (3)$$

Due to low energy treatment for these chemical reaction, the way to approach CO_2 conversion process by non-thermal plasma discharge can be performed and the high CO_2 conversion in this plasma technique will be studied in this work by following experimental set up below.

Experimental set up

The experimental set up was carried out as shown in Fig. 1 which the system consisted of sample feed tanks of purified CO_2 and Ar gas and their accessories (gas regulator, butterfly valve, flow meter, mixer unit, needle valve), coaxial DBD reactor, bubble flow meter, high voltage power supply. For measurement, high voltage (HV) probe (Tektronix, P6015A) which was crossed between high voltage line and ground the resistor and connected to digitized storage oscilloscope (Tektronix, TDS3014B), was used for detection HV input of DBD reactor while the charge transfer can be measured from voltage across C_m by using voltage probe. These parameters of applied voltage and charge transfer were utilized to calculate the power consumption by Q-U Lissajous plotting [26]. The mixing gas before and after treatment by quartz tube DBD in each operating condition was evaluated by gas analyzer (Geotech, Biogas Check). A quartz tube 1 mm of thickness with inner diameter 12 mm was provided as DBD plasma reactor. Both flanges closing reactor tube was made of Teflon insulator and used for stainless steel inner electrode support to protection HV shock and outer electrode was made of Aluminum flat sheet wrapping around the tube while stainless steel rod is placed at center of the quartz tube and acted as inner electrode.

Effect of discharge gap and two outer electrodes, CO_2 concentration, outer electrode length and applied voltage on CO_2 decomposition were evaluated and presented in the next section.

To evaluate the performance of the DBD system for CO_2 decomposition, the percentage of CO_2 conversion (χ_{conv}), O_2 selectivity (O_{2s}), power consumption and conversion efficiency were determined by following Eq. 4 and 5, respectively. The following equation for calculating of CO_2 conversion and O_2 selectivity can be written as below [15, 24].

$$\chi_{\mathrm{conv}}\ (\%) = \frac{\mathrm{CO_2\ converted\ (mol)}}{\mathrm{CO_2\ input\ (mol)}} \times 100 \qquad (4)$$

$$\mathrm{O_{2s}}\ (\%) = \frac{\mathrm{O_2\ product\ (mol)}}{\mathrm{CO_2\ converted\ (mol)}} \times 100 \qquad (5)$$

Additionally, the power consumption (P_E) can be determined by integrating energy consumption during operating period as illustrated in Eq.6 while the conversion efficiency (η_{conv}) from Eq. 7 has been adopted from the previous works [2, 26] as shown below.

$$\mathrm{P_E\ (W)} = \mathrm{f} \cdot \mathrm{C_m} \int_0^T \mathrm{U_t du_c} \qquad (6)$$

$$\eta_{\mathrm{conv}}(\%/\mathrm{W}) = \frac{\mathrm{CO_2\ conversion\ (\%)}}{\mathrm{P_E\ (W)}} \qquad (7)$$

where f = fixed frequency of power source used, kHz
C_m = certain measuring capacitor which was used for determining voltage drop by voltage probe
U_t = applied voltage, V
u_c = voltage across certain measuring capacitor, V

In this experiment the frequency of power source was fixed at 7.8 kHz and the certain measuring capacitor was fixed at 10 nF.

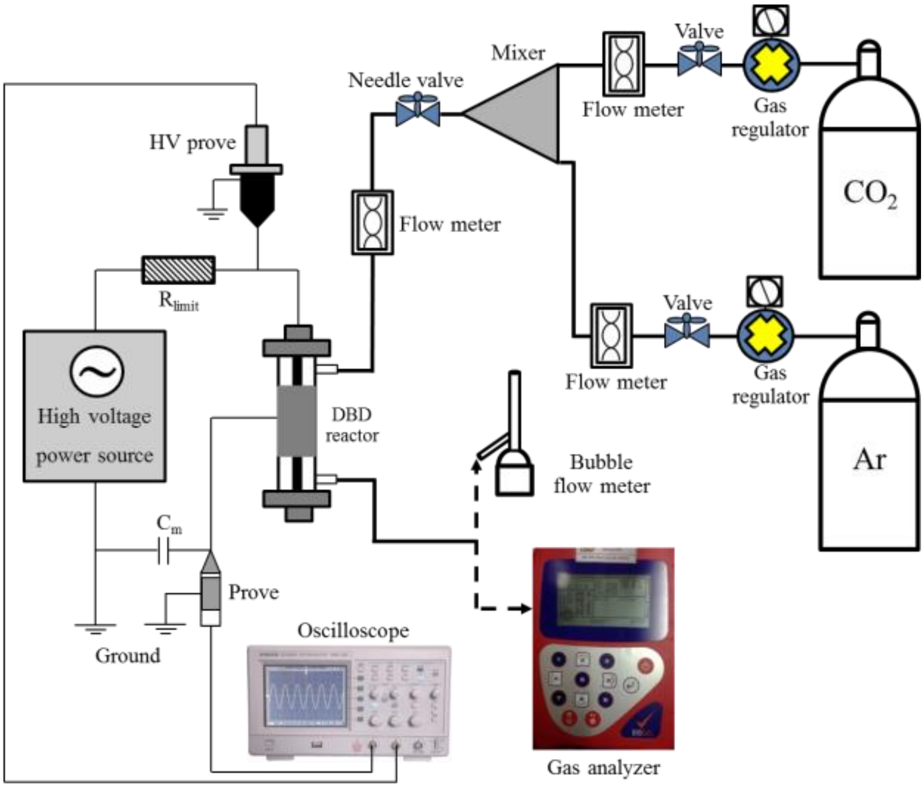

Figure 1. *Experimental set up of CO_2 conversion process by plasma dielectric barrier discharges*

Results and discussion

Characteristic of Plasma in DBD system

To verify the DBD system on its configuration before doing each experiment, the DBD system was constructed following on the Fig. 1. However, studying effect of electrode shape configuration, the two outer electrode shapes configuration were proposed in this research and tested at the same operating conditions (power supply of 8 kV 7.8 kHz). Fig.2 illustrated corona discharge pattern of the two different outer electrode shape configuration which was installed into single part outer electrode shape (Fig. 2A) and double parts outer electrodes shape (Fig. 2B), respectively. From the figures its non-thermal plasma discharges of the two electrode shapes configuration was similar pattern with purple color corona discharges. This is because the gas inlet flowing pass through DBD gap was ambient air which is mostly consists of nitrogen gas (atmospheric pressure) [8, 12].

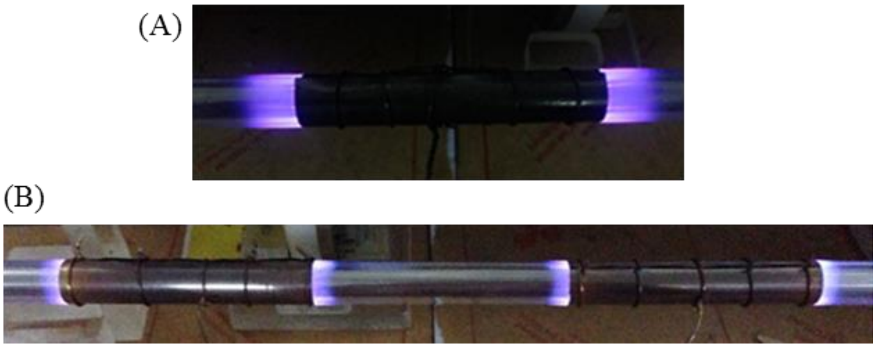

Figure 2. *Corona discharge of DBD plasma reactor with single part outer electrode shape (A) and double parts outer electrodes shape (B) with distance apart of 8 cm*

The consumed energy in the reactor was determined by voltage–charge curve (V–Q Lissajous figure). In the previous experiment [15], the consumed energies obtained with V–Q Lissajous figure were checked by comparing with the values calculated from the time integral of the product of the applied voltage and the current [16]

Effect of CO_2 concentration

To study effect of CO_2 concentration on CO_2 conversion and O_2 selectivity, the purified CO_2 gas and Ar gas were feed in to mixing tube using ranging between 60% and 90% by volume. The accurate mixing gas flow rate was controlled by needle valve and fixed at 50 ml/min while discharge gap of 1.30 mm width, and outer electrode length of 8 cm and applied voltage across the electrodes was about of 8 kV. By calculation with Eq.(4) and Eq.(5), plotting graph between CO_2 conversion and concentration of CO_2 was illustrated in Fig.3. The experimental results showed that the increase of CO_2 concentration causes CO_2 conversion decreased. On the other hand, O_2 selectivity which was the gas product has higher increased at 80% of CO_2 concentration. The low mixing ratio of CO_2 concentration replied that a high amount of Ar plasma discharges increased the collision of gas reaction in discharge zone between electrodes. This is because Ar after breakdown (as plasma state) provides more electrons and ions. This result is corresponded to the previous research works [1, 11-12, 21].

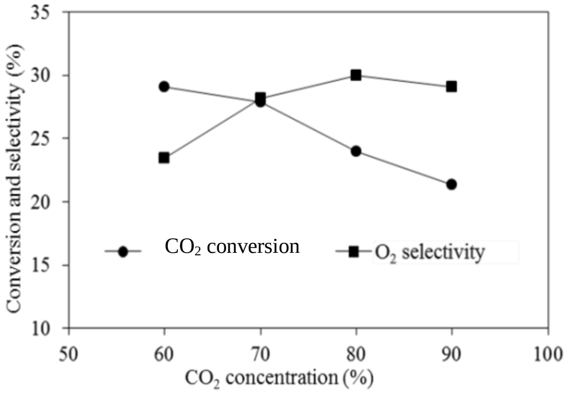

Figure 3. *Effect of CO_2 concentration on CO_2 conversion and O_2 selectivity*

Effect of electrode configuration and applied voltage

To study effect of electrode configuration on CO_2 conversion. the experimental condition was carried on certain conditions of 50 ml/min of gas flow rate and percentages of mixing ratio of CO_2 and Ar at 60:40. Two types of DBD plasma reactor with single part outer electrode shape and double parts outer electrodes shape outer electrodes configuration were shown in Fig. 2(a) and 2(B), respectively. Moreover, the Ar plasma discharge between coaxial discharge gap between inner and outer electrodes were chosen at 1.3 mm and 2.8 mm of spacing gap (Fig. 5), respectively. Then the experimental results of CO_2 conversion and O_2 selectivity were plotted along with applied voltage cross electrodes and 2 different discharge spacing gap of 1.3 and 2.8 mm. as illustrated on Fig. 4 and Fig.5, respectively. The results showed that the percentage of CO_2 conversion (Bold line in Fig.4 and Fig.5) and percentage of O_2 selectivity (dot line in Fig.4 and Fig.5) were relatively affected by the applied voltage and outer electrode length whilst the discharge spacing gap gave a little effect to the percentage of CO_2 conversion and percentage of O_2 selectivity comparing to the parameters mentioned above. In addition, the Ar plasma discharge occurring at discharge gap for 8 cm and 10 cm of outer electrode lengths tended to increase percentage of CO_2 conversion because the longer outer electrode length had a long period of CO_2 dissociation. The conclusion was stated that the applied voltage across electrodes and outer electrode length significantly affected to increasing of percentage of CO_2 but low affected to percentage of O_2 selectivity.

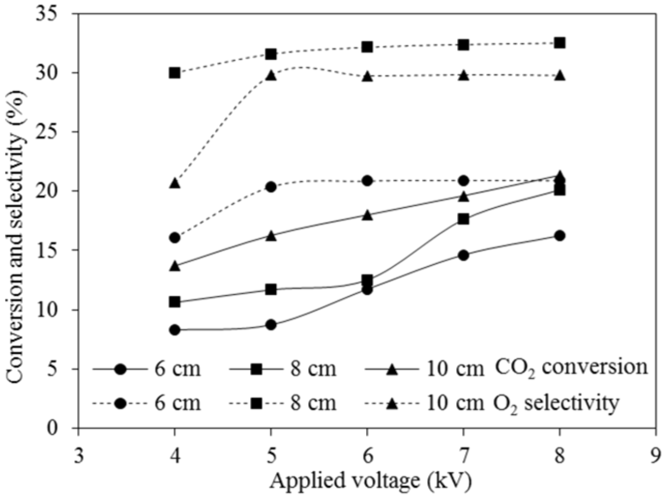

Figure 4 Effect of outer electrode length and applied voltage on CO_2 conversion and O_2 selectivity at 1.3 mm of discharge gap

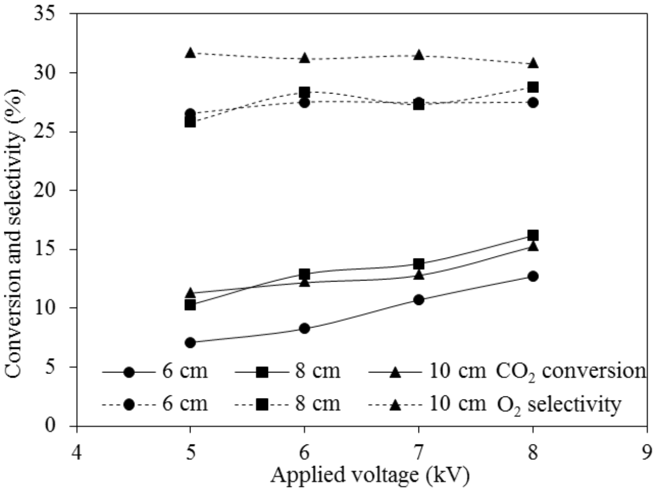

Figure 5 *Effect of outer electrode length and applied voltage on CO_2 conversion and O_2 selectivity at 2.8 mm of discharge gap*

To clarify effect of discharges spacing gap and outer electrode shape on percentage of CO_2 conversion and percentage of O_2 selectivity, the experiments were run and illustrated on Fig.6 and Fig.7, respectively. The discharge spacing gap was varied between 0.4 mm and 2.8 mm and outer electrode length of 8 cm, gas flow rate of 50 ml/min and high percentage mixing ratio of CO_2:Ar at 80:20. Fig.6 illustrated relationship between percentage of CO_2 conversion and applied voltage across electrodes at 3 different discharge gaps. The experimental results showed that the percentage of CO_2 conversion is the highest value at discharge spacing gap of 1.3 mm especially on the double outer electrodes shape with 1.3 mm of discharge gap (1.3 mm, 2OE on Fig.6)

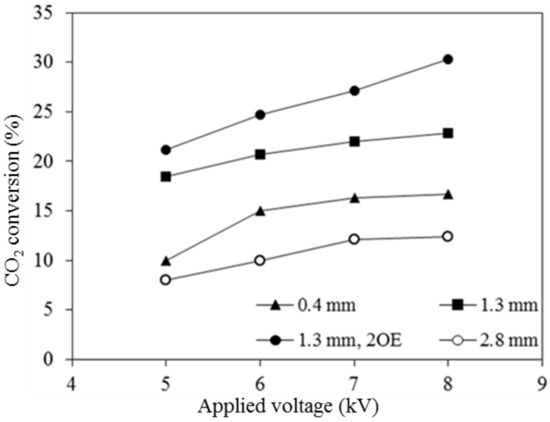

Figure 6. *Effect of discharge gap and two outer electrodes (2 OE) on CO_2 conversion*

Due to determine percentage of O_2 selectivity, the result was illustrated on Fig. 7 which could be stated that the percentage of O_2 selectivity using discharge gap of 1.3 mm width slight decreased when the applied voltage increase.

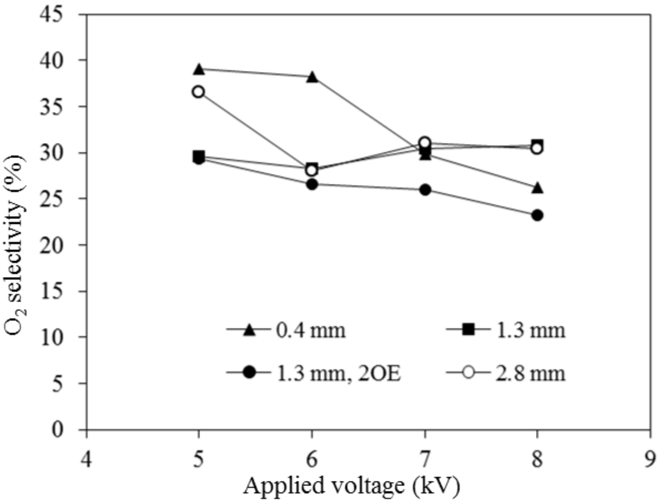

Figure 7. *Effect of discharge gap and two outer electrodes (2 OE) on O_2 selectivity*

Power consumption and conversion efficiency

From Eq.(6) and Eq.(7), the energy consumption and conversion efficiency can be determined and showed in Fig.8-10. The percentage of CO_2 conversion increase with increase of applied voltage across both electrodes and increase of mixing gas flow rate. Fig.8 stated that the energy consumption of plasma discharges system increased with increase of applied. On the other hand, the percentage of conversion efficiency decreased when an applied voltage increased. However, the result has indicated that the high efficiency of CO_2 conversion can be achieved at 1.3 mm of discharge gap of single outer electrode and 1.3 mm of discharge gap with double outer electrodes as shown in Fig.9 and Fig.10.

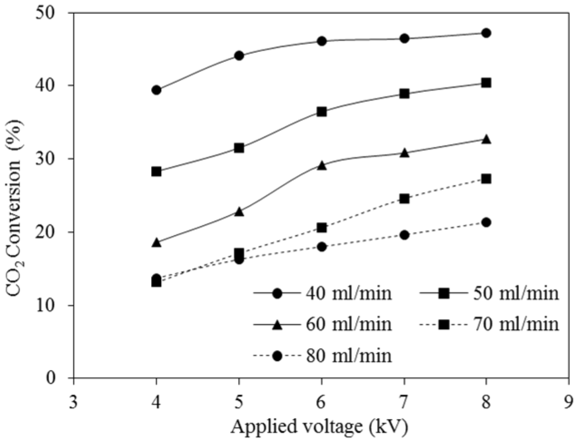

Figure 8 *Effect of gas flow rate and applied voltage on CO_2 conversion and O_2 selectivity*

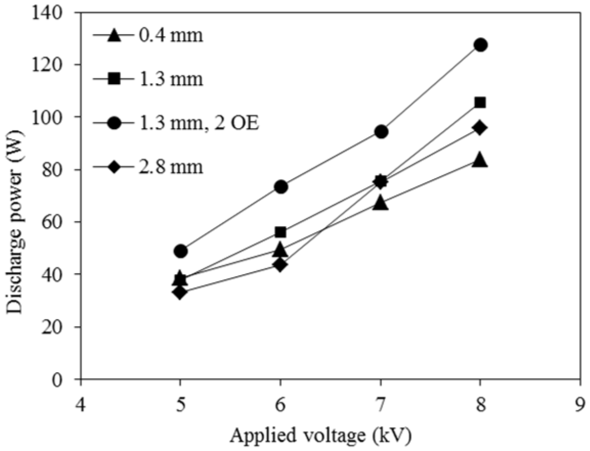

Figure 9 *Discharge power versus applied voltage for each discharge gap*

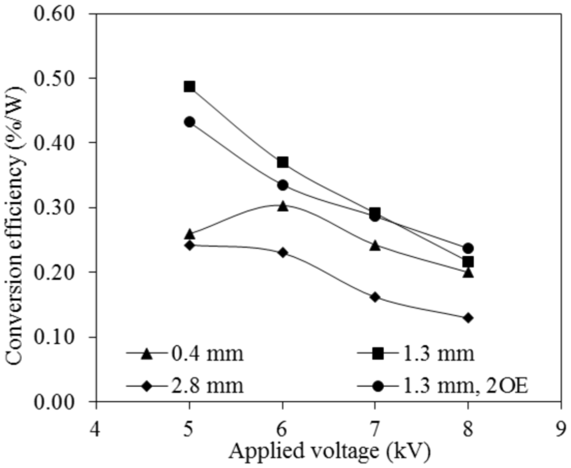

Figure 10 *Conversion efficiency versus applied voltage for each discharge gap*

Conclusion

In summary, this research work had obviously exhibited that the use of the longer outer electrode and double outer electrodes configuration with narrow discharge gap had high performance comparing to the other operating condition. It replies that plasma dielectric barrier discharge system can be used for enhancing CO2 conversion. In similarity, the increase of applied voltage across electrodes and the lower flow rate of mixing gas can also improvable technique for enhancing percentage of CO_2 conversion.

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