Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Hazardous Materials 146 (2007) 309–315
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Gliding arc plasma processing of CO_2 conversion

Antonius Indarto [a,b,*], Dae Ryook Yang [a], Jae-Wook Choi [b], Hwaung Lee [b], Hyung Keun Song [b]

[a] *Department of Chemical and Biological Engineering, Korea University, Anam-dong, Sungbuk-gu, Seoul 136-701, South Korea*
[b] *Korea Institute of Science & Technology, Clean Technology Research Center, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea*

Received 17 December 2005; received in revised form 15 October 2006; accepted 7 December 2006
Available online 15 December 2006

Abstract

Conversion of carbon dioxide (CO_2) using gliding arc plasma was performed. The research was done to investigate the effect of variation of total gas flow rates and addition of auxiliary gases – N_2, O_2, air, water – to the CO_2 conversion process. This system shows higher power efficiency than other nonthermal plasma methods. Experiment results indicate the conversion of CO_2 reaches 18% at total gas flow rate of 0.8 L/min and produces CO and O_2 as the main gaseous products. Among auxiliary gases, only N_2 gives positive effect on CO_2 conversion and the power efficiency at N_2 concentration of 95% and total gas flow rate of 2 L/min increases about three times compared to pure CO_2 process.

Keywords: Plasma; Gliding arc; CO_2 conversion; Power efficiency

1. Introduction

Gliding arc plasma can be easily characterized by the presence of the flame between the discharge gap of two metal electrodes. This flame is created as an effect of arcs movement on the surface of electrodes (sliding) caused by high velocity of penetrated gas. It has received attention from many scientists for the application in chemical reactions, such as pollutant decomposition, etc. [1]. Although gliding arc plasma is classified as cold plasma, some characteristics of thermal (hot temperature) plasma exist. Song et al. mentioned the plasma-combustion process as simultaneously occurring in gliding arc plasma process [2]. This characteristic is one advantage of decomposing toxic and dangerous gases that usually have strong bond or chemical structure, such as CO_2.

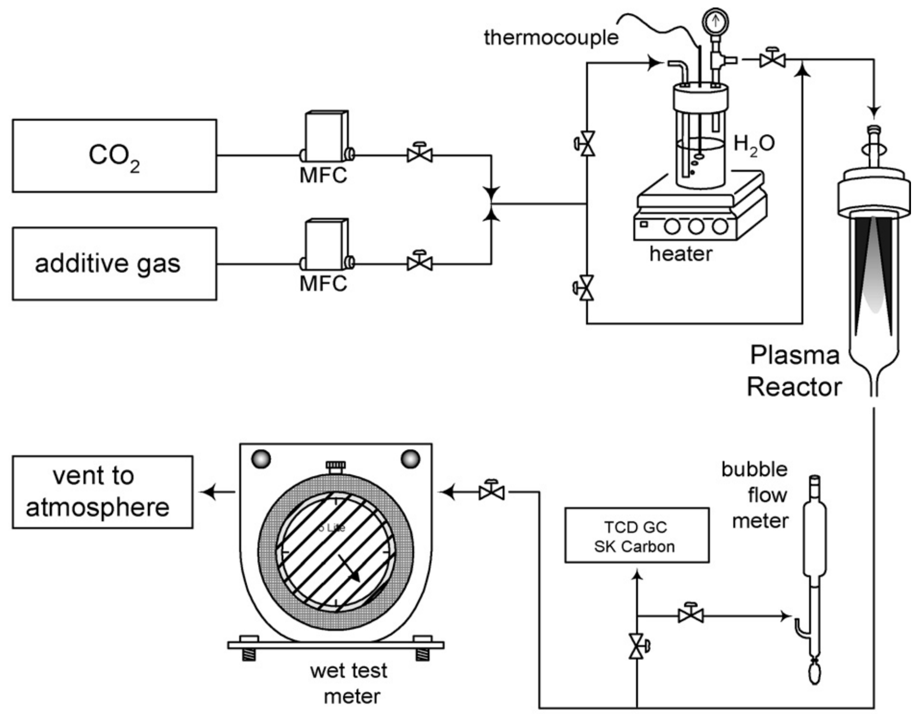
CO_2 is a well-known source of green house gas that contributes to the climate change [3]. Concerning this situation, Kyoto protocol obliges industrialized countries to cut their greenhouse gases emissions by an average 5.2% between 2008 and 2012. Currently, around 2×10^{15} g per annum of CO_2 is being released to the atmosphere from many sources. This situation indicates a clear need to find effective methods to reduce CO_2 emissions. The industrial sector has been suspected as the main contributor on emitting CO_2 to the ambient air [4,5]. Thermodynamic calculation shows that the chemical bond of CO_2 begins to crack at 1500 °C and it will be completely broken at temperature >5000 °C. It means high energy has to be supplied to the system to achieve the required process temperature.

In recent years, some studies were carried out on plasma-assisted methods for direct conversion of CO_2, such as radio frequency (RF) plasma [6], corona [7,8], dielectric barrier discharge (DBD) [9], glow discharge [10,11], and thermal plasma [12]. Although in their papers, the authors claimed high conversion rate has been achieved, the energy efficiency of these processes was relatively low. Except for thermal plasma, their proposed systems can only handle small flow rates.

In this study, gliding arc plasma, as one of the advanced methods which is believed can produce numerous amounts of energetic radical species and capable to treat high emission flows, was applied to decompose CO_2. Compared to the previous plasma methods, gliding arc plasma has a great chance to be utilized for industrial chemical reactions [13]. In our previous experiments, methane conversion [14,15] and decomposition of chloromethane [16–19] has been done successfully using the gliding arc plasma. Plasma-combustion process produces high

* Corresponding author at: Clean Technology Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea. Tel.: +82 10 2296 3748.
E-mail address: indarto_antonius@yahoo.com (A. Indarto).

0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2006.12.023



Note: MFC = mass flow controller

Fig. 1. Schematic diagram of experimental setup.

plasma flame temperature and can be an advantage for destructing toxic and hazardous compounds.

2. Experimental setup

The schematic diagram of the experimental setup is shown in Fig. 1. CO_2 was used as the main input gas with purity of 99% and controlled by a mass flow rate controller (Tylan, FC-280S). The total flow rates were varied from 0.85 to 2 L/min. Some auxiliary gases, e.g. O_2, N_2, air, were also injected to study their effects on the CO_2 conversion and reactions. The flow rate was also controlled by the same specification of mass flow controller. To produce water vapor, some portions of CO_2 were injected to the water body and the amount of produced water vapor was controlled by maintaining the temperature and pressure of the chamber. The composition of the outlet mixture was analyzed before and after plasma reaction. Before analysis by gas chromatography (GC), the flow rate of gas sample was measured first by a bubble flow meter. The fluctuation of flow rate, which was caused by compression and expansion of gas volume due to reactions, was measured by a wet test meter (Ritter-German, 5 L capacity).

The reactor was made from a quartz-glass tube that has inner diameter of 45 mm and length of 250 mm. The upper part of reactor was covered with a Teflon seal and two 150 mm in length of triangle electrodes made from stainless steel stuck on it. The separation of electrodes in the narrowest gap was only 1 mm. The gas mixture was introduced between the electrodes by a capillary tube with inner diameter of 0.3 mm. A high frequency AC power supply (Auto electric, A1831) was connected to the gliding arc electrodes. The maximum voltage was 10 kV and current was 100 mA. Fig. 2 shows the waveform pattern of voltage and current used in this study. It shows that there was a waveform transformation before and after plasma turned on. At the steady-state plasma condition after breakdown point, the voltage got lower than the adjusted original voltage. On the other hand, the current value increased and higher than that before breakdown. This phenomenon was caused by arcs production in the plasma, which typically occurred at low voltages and high currents condition.

The concentration of CO_2, CO, and O_2 in the gas mixture before and after the reaction was determined by GC (YoungLin M600D, Column: SK Carbon, thermal conductivity detector). To evaluate the performance of the process, CO_2 conversion and products selectivity were calculated and defined as:

$$\text{Conversion of } CO_2\,(\%) = \frac{\text{converted } CO_2}{\text{initial } CO_2} \times 100 \tag{1}$$

$$\text{Selectivity of CO}\,(\%) = \frac{\text{CO formed}}{2 \times \text{converted } CO_2} \times 100 \tag{2}$$

$$\text{Selectivity of } O_2\,(\%) = \frac{O_2 \text{ formed}}{\text{converted } CO_2} \times 100 \tag{3}$$

Power efficiency terminology was used as the way to measure the system efficiency and calculated as:

$$\text{Power efficiency} = \frac{\text{total converted } CO_2}{\text{supplied power}} \tag{4}$$

The supplied power was calculated by integration calculation of voltage and current wave captured by oscilloscope

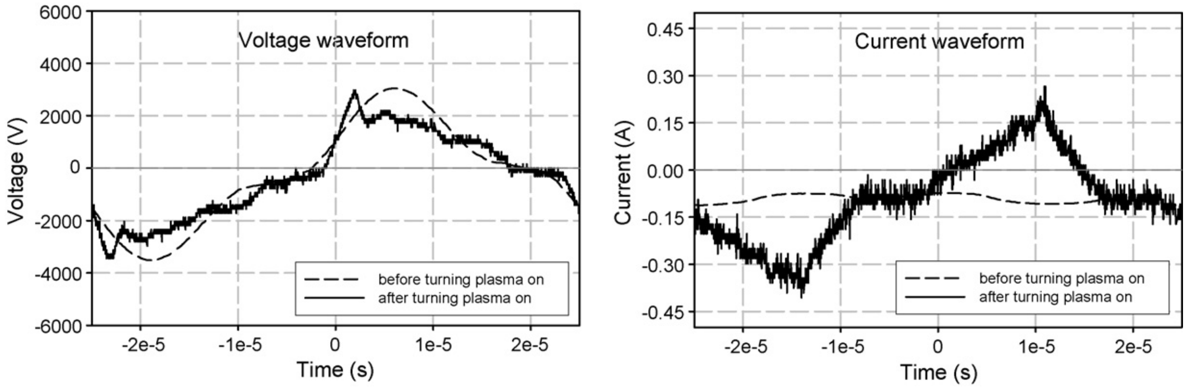


Fig. 2. Applied voltage and current waveform.

(Agilent 54641A).

$$\text{Supplied power} = \int (V(t) \times I(t))\, \mathrm{d}t \times \text{frequency} \tag{5}$$

3. Result and discussion

3.1. Effect of gas flow rate of pure CO_2 stream

The effect of various gas flow rates, related to the residence time of CO_2 molecule in the reactor, was examined. Fig. 3(a) shows the CO_2 conversion difference affected by flow rates change at the frequency of 20 kHz. As the total flow rates increase, the conversion of CO_2 tends to decrease. Higher flow rates reduce the residence time of CO_2 molecule in the reactor and also reduce the opportunity and time of CO_2 to collide with electrons and other high-energy state species. Those species, especially electron, have enough energy to destroy the carbon–oxygen bond [20].

Fig. 3(b) shows the selectivity of CO and O_2 as the main products of the plasma reaction in gliding arc. The selectivity of CO reaches about 30% and O_2 reaches about 35%. However, the ratio calculation of oxygen-atom in the outlet and input stream of this experiment is close to (1). This result supports our previ-

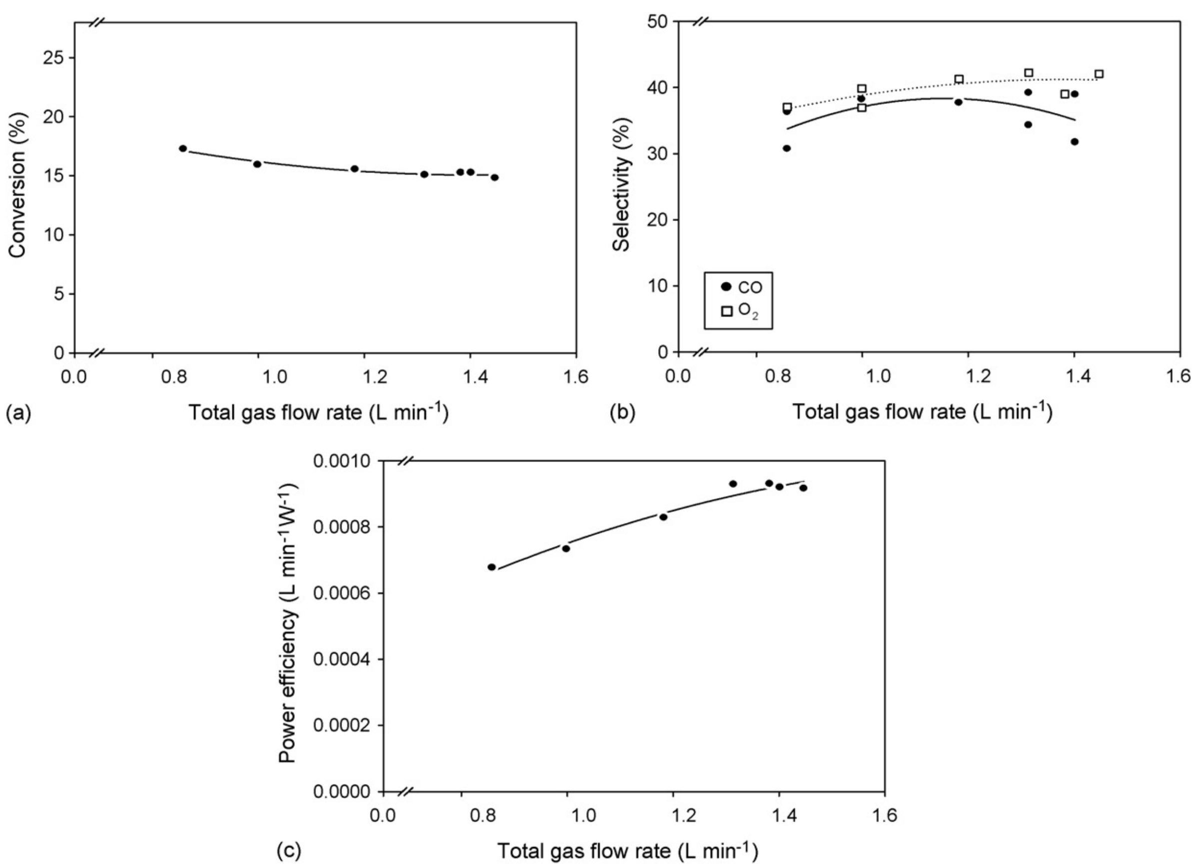


Fig. 3. Effects of total gas flow rate on (a) CO_2 conversion, (b) product selectivity, and (c) power efficiency. The experiment was conducted at pure CO_2 condition and fixed frequency of 20 kHz.

ous statement that CO and O_2 were found as the main products. It is a good experimental result because O_2 is more valuable and useful gas compared to CO_2 and CO can be mixed with H_2 to form synthesis gas. Although CO is also categorized as toxic gas, CO molecule is more reactive than CO_2 and makes a higher possibility to be converted into another higher valuable product.By reaction with electron, the initiation of plasma reaction could be separated into two kinds of reactions [20]: (i) direct reaction which produced CO and O_2,

$$CO_2 + e \rightarrow CO + O + e \quad (6)$$

$$CO_2 + e \rightarrow C^+ + O_2 + 2e \quad (7)$$

and (ii) intermediate reaction which produced high energetic intermediate species and ions. Our kinetic simulation shows that O, O_2^+, and CO^+ have an important role to govern the way of reactions [21]. Instead of direct reaction e with CO_2, O_2 could be produced by reactions of those radical species and ions via O_3,

$$O + O_3 + M \rightarrow 2O_2 + M \quad (8)$$

$$O + O_3 \rightarrow 2O_2 \quad (9)$$

or recombinant process,

$$O_2^+ + CO_2 + e \rightarrow CO_2 + O_2 \quad (10)$$

CO^+ has significant role in production of CO by,

$$CO^+ + O \rightarrow CO + O^+ \quad (11)$$

$$CO^+ + CO^2 \rightarrow CO + CO_2^+ \quad (12)$$

However, although the CO_2 conversion decreases with increasing total gas flow rates, the efficiency of power has increased (Fig. 3(c)). It means more CO_2 molecules have been converted in higher gas flow rates rather than in lower ones. The power efficiency will increase 6.4% per 100 mL increment of gas flow rates. In this process, the supplied power to the reactor was around 218 W at gas flow rate of 0.85 L and rises 2.48 W per 100 mL increment of gas flow rate. Increasing supplied power is caused by higher breakdown power to produce arcs in higher gas flow rates. This phenomenon has been investigated before [22].

3.2. *Effects of auxiliary gases*

The effects of air, O_2, and N_2 on CO_2 conversion have been studied also. Fig. 4 shows the curve trend of CO_2 conversion, CO selectivity, and power efficiency at a total gas flow rate of 2 L/min and a frequency of 20 kHz. As shown in Fig. 4(a), higher CO_2 conversion was found when N_2 existed in the input stream. The conversion rises as the concentration of N_2 increases. The increasing rate at 95% volume of N_2 reaches about 2.5 times higher than that at only CO_2 injection. The effect of N_2 in the process has been studied before and it shows that at higher concentration, N_2 molecules have higher possibility to contribute in the reaction mechanism by excitation of N_2 molecules [23]. The excitation of N_2 into higher vibrational level and meta-stable state (N_2(A) and N_2(a′)) will help to increase the conversion of CO_2.

Interesting result was found when O_2 was diluted in the input stream. Although O_2 is a well-known oxidant gas that is very efficient to decompose toxic compounds in combustion process, Fig. 4 shows that the CO_2 conversion is below the conversion of pure CO_2. In the plasma reaction, the existence of exited O_2 both in neutral or ion state will govern some reverse reactions of C to CO_2:

$$C + (O_2)^* \rightarrow CO_2 \quad (13)$$

$$C + (O_2{}^-)^* \rightarrow CO_2 + e \quad (14)$$

$$C + (O_2{}^+)^* + e \rightarrow CO_2 \quad (15)$$

or from CO by exited single O or radical ($O^\bullet$)

$$CO + O^* \rightarrow CO_2 \quad (16)$$

Although it is believed that O_2 has some excitation metastable levels [24], the potential energy is relatively small to be transferred, only 0.98 eV from $a^1\Delta_g$ and 1.63 eV from $b^1\sum_g{}^+$ to the ground state [25]. In case of photoionization process, O_2 requires more power to transfer into higher energy level compared to CO_2. The bond energy comparison also shows that O_2 is more difficult to be cracked than CO_2. Those will effect on the reducing number of ion and active species in the plasma system. Decreasing conversion of target material, which is caused by existing of O_2 in the plasma process, was also found in chloromethane decomposition [26].

Using atmospheric air as the auxiliary gas mixture, CO_2 conversion curve is close to the O_2 results. The effect of some existing impurities can be negligible because the concentration is in trace level. It can be said that the plasma reaction process will be a mixed combination of N_2 and O_2 process. When it is compared with pure CO_2 conversion, the overall conversion is lower. It shows that, although the conversion of CO_2 can increase because of N_2, the existing of exited oxygen species give dominant effect by reverse CO_2 production reaction in the plasma process. A report suggests that O_2 molecules increased the conversion of CO_2 in few concentrations [27], but unfortunately, we could not afford those ranges in this experiment.

Fig. 4(b) shows the effect of auxiliary gas contents on the production of CO at total flow rate of 2 L/min. The conversion of CO_2 to CO reaches 35%. The existence of O from O_2 can help to increase the selectivity of CO when it collides with C by [25]:

$$e + O_2 \rightarrow O^+ + O + 2e \qquad \text{(dissociative ionization)} \quad (17)$$

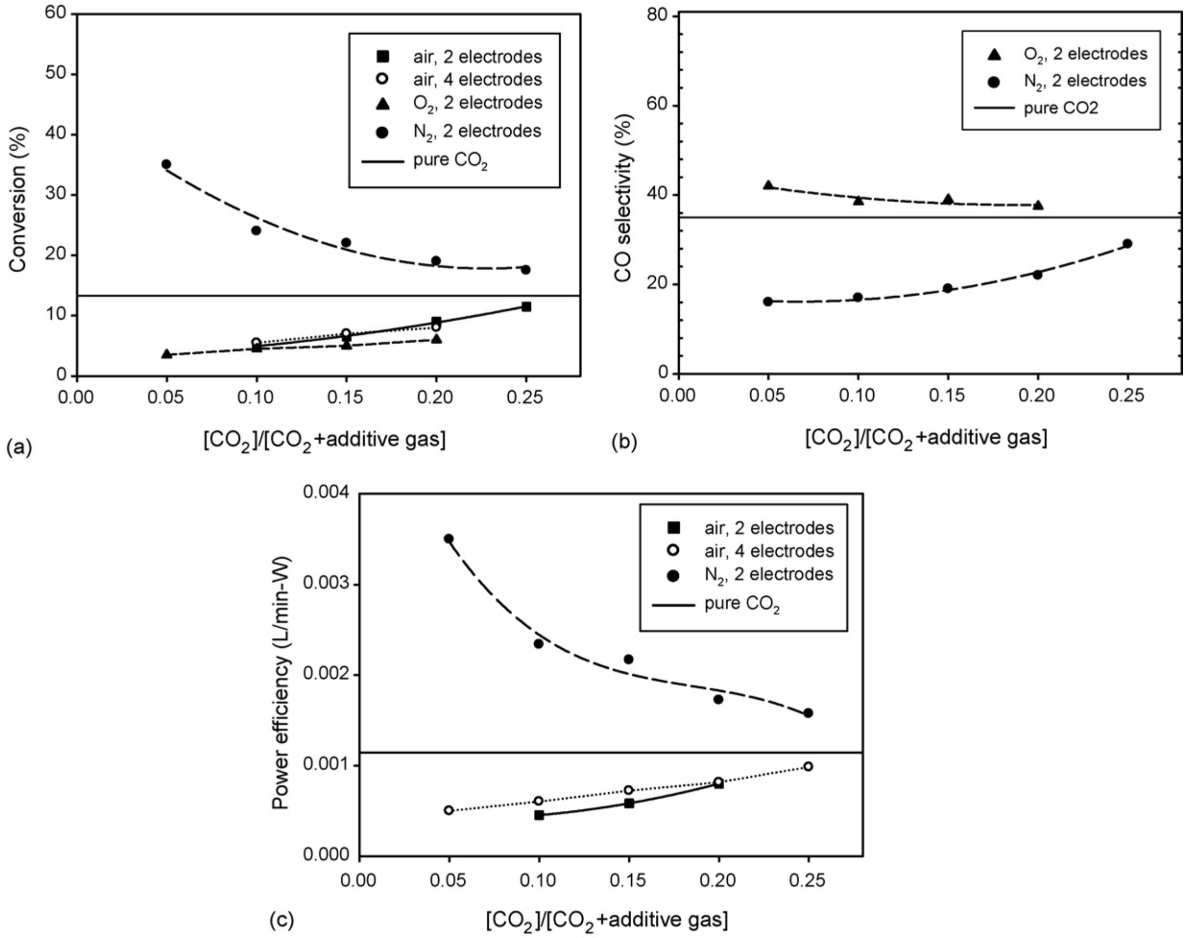
$$e + O_2 \rightarrow O^- + O \qquad \text{(dissociative attachement)} \quad (18)$$

$$e + O_2^\bullet \rightarrow {}^\bullet O^- + O^+ + e \quad \text{(dissociative attachement)} \quad (19)$$

$$e + O_2^\bullet \rightarrow {}^\bullet 2O + e \qquad \text{(dissociation)} \quad (20)$$

and

$$C + \langle O \rangle \rightarrow CO \quad (21)$$



Note: 2 electrodes mean 1 anode and 1 cathode, 4 electrodes mean 2 anodes and 2 cathodes

Fig. 4. Effects of auxiliary gases on (a) CO_2 conversion, (b) CO production, and (c) power efficiency. The experiment was conducted at fixed flow rate of 2 L/min and frequency of 20 kHz.

⟨···⟩ means that it can be in active states: excited neutral/ion or radical.

On the other hand, nitrogen species in any forms and energy levels can reduce the probability of C to be CO. Nitrogen has a possibility to react with single O or double O atom and converts into NO, N_2O, and NO_2 [28], although in the analysis results the selectivity of those compounds was relatively low.

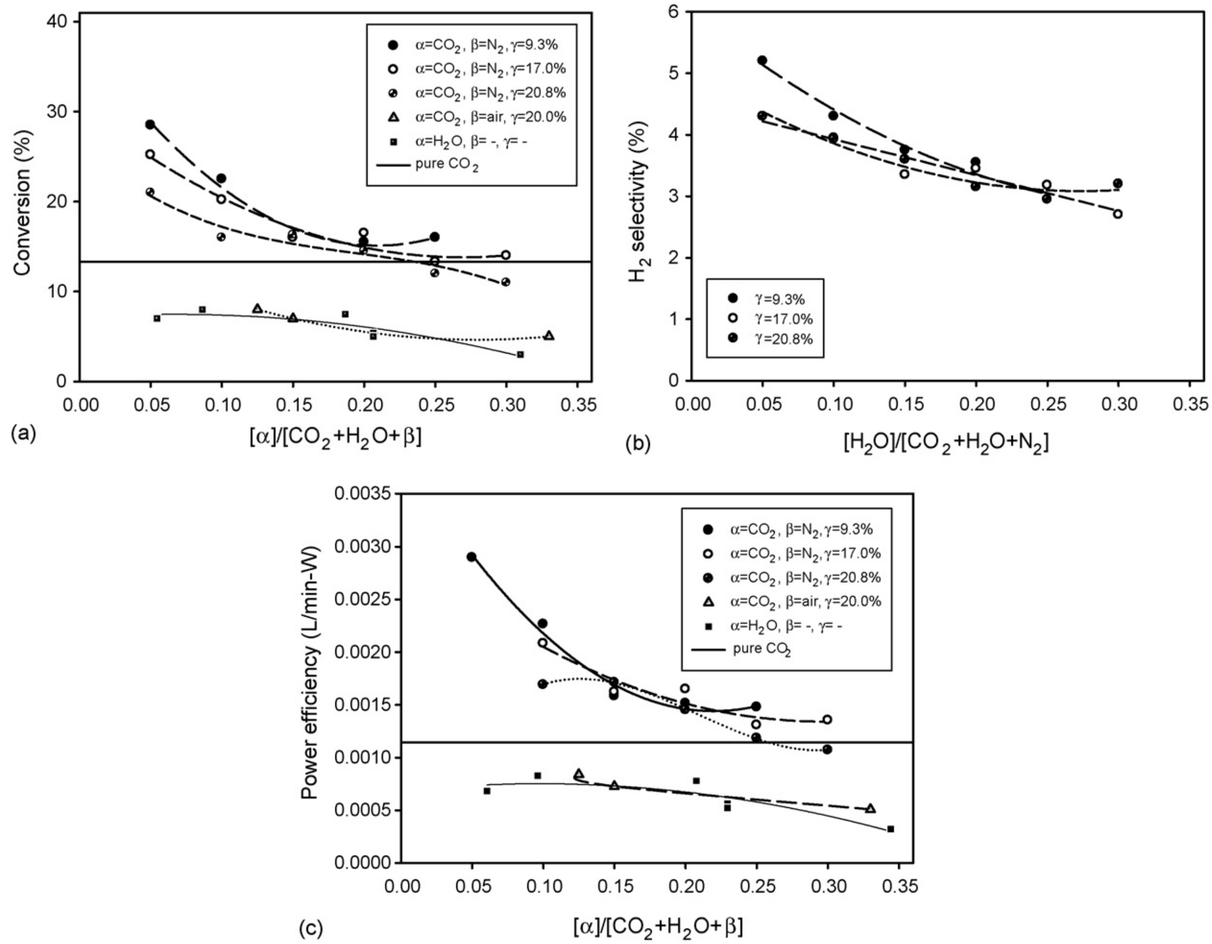
The existence N_2 in the system increased the efficiency of the process of CO_2 conversion also. At N_2: CO_2 = 95:5, the power efficiency increased about 3.2 times compared to the pure CO_2 process. Instead of increasing the CO_2 conversion, N_2 gives a significant effect on reducing the consumed power of plasma. At high concentrations of N_2 (>75%), the rate of power reduction reaches about 5.5 W for every 5% concentration increment of N_2 in the input stream. Air and O_2 show the opposite experimental result. The efficiency decreases when those compounds exist in the plasma process.

3.3. Effects of water vapor

The possibility to produce some gaseous fuel products such as H_2 and CH_4 by CO_2 and H_2O reaction, which is still challenging [29] has been tested by addition of water vapor. Fig. 5(a) shows the addition of water vapor in the input stream, without another auxiliary gas, decreased the conversion of CO_2 in all ranges of experiments. In our observation, moisture water made the gliding plasmas unstable and the instability increased with the increasing water vapor concentration. This could be the reason why the conversion decreased. Generally, the conversion was less than 10%.

In order to increase the conversion rate, N_2 was added in the system. By addition of N_2, the conversion increases and higher than the conversion at pure CO_2 injection. The highest conversion is occurred at H_2O:CO_2:N_2 = 0.05:0.055:0.94, or at the highest concentration of N_2 and the lowest concentration of H_2O. When this result is compared to Fig. 4(a), although the concentration of N_2 is little bit different, it can be concluded that reducing conversion which is caused by water is more dominant in the plasma reaction. For example, at 95% of N_2 concentration in Fig. 4(a), the conversion reaches 35% while in Fig. 5(a), at similar condition, the conversion is only 29%. In gliding arc plasma, the physical characteristic of water might be similar to atmospheric air. When N_2 is changed with air (Fig. 5(a)), the conversion value is almost same.

The possibility of H_2O conversion into H_2 was also investigated. The mixing ratio was exactly similar to the previous



Note: $\gamma = \frac{[H_2O]}{[N_2]}$ in vol/vol dimension

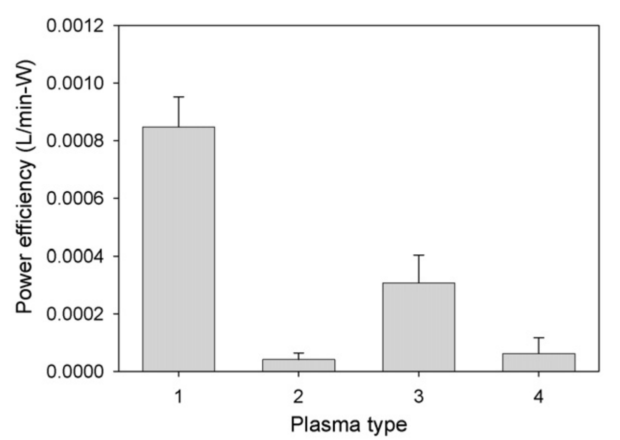
Fig. 5. Effects of water vapor on (a) CO_2 conversion, (b) H_2 production, and (c) power efficiency. The experiment was conducted at fixed flow rate of 2 L/min and frequency of 20 kHz.

system where N_2 was used as the second auxiliary gas. Without N_2, the conversion of water was small and H_2 product could not be detected well in our GC system. Fig. 5(b) shows the selectivity of H_2. Unfortunately, the selectivity is not exceeding 6% in all ranges of experiment.

Instability of plasma caused by water vapor has reduced the process efficiency (Fig. 5(c)). The lowest power efficiency occurred at the highest concentration of water vapor. However, by adding another auxiliary gas such as N_2, it will help the process efficiency and can be higher that pure CO_2 conversion.

3.4. Comparison with other plasma systems

In order to check the performance of gliding arc plasma, some other references of nonthermal plasmas have been compared. Fig. 6 shows power efficiency of this experiment is significantly higher than when it is conducted by corona discharge [5]. Although the conversion percentage is relatively same compared to the DBD discharge, this system can handle higher input flow rate (∼40× higher) [30].



Note: [1]Gliding Arc Plasma (this experiment), [2]Plate DBD (ref. 30), [3]Tube DBD (ref. 10), [4]RF plasma (ref. 31)

Fig. 6. Power efficiency comparison among nonthermal plasmas [10,30,31].

4. Conclusion

The performance of CO_2 decomposition in gliding arc plasma at atmospheric pressure was studied. Some additional gases were used to investigate the conversion efficiency. Proved by the similarity between experimental and simulation result, the conversion reaction was initiated by electron. The existence of excited N_2 level gives a positive effect while O_2 and air produce an opposite effect, which might be caused by reverse reaction C and CO to CO_2. The conversion of CO_2 reaches 35% at N_2 concentration 95%, higher that pure CO_2 injection conversion which is only 15–18%. The plasma reaction produces CO and O_2 as the main products. Existing water in the plasma reaction decreases the CO_2 conversion and the selectivity of H_2 from water is less than 6%. Although this process shows better performance than other nonthermal plasma systems, some process modifications should be done, for example catalyst addition, to enhance better experimental results.

Acknowledgments

This study was supported by the National Research Laboratory program of the Korea Ministry of Science and Technology. The first author would like to thank the Korea Institute of Science and Technology and the Korea University for their support.

References

[1] A. Czernichowski, Gliding arc: applications to engineering and environment control, Pure Appl. Chem. 66 (1996) 1301.

[2] Y.-H. Song, M.-S. Cha, K.-T. Kim, Y.-H. Kim, S.-J. Kim, Comparison study of plasma generation technique for treating pollutant gases, Proceedings of the 5th International Symposium on Pulsed Power and Plasma Applications, 2004, pp. 404–407.

[3] J.J. Shah, H.B. Singh, Distribution of volatile organic chemicals in outdoor and indoor air, Environ. Sci. Technol. 22 (1998) 1381.

[4] B. Kiani, Y. Hamamoto, A. Akisawa, T. Kashiwagi, CO_2 mitigating effects by waste heat utilization from industry sector to metropolitan areas, Energy 29 (2004) 2061.

[5] N. Yabe, An analysis of CO2 emissions of Japanese industries during the period between 1985 and 1995, Energy Policy 32 (2004) 595–610.

[6] S.Y. Savinov, H. Lee, H.K. Song, B.K. Na, Decomposition of methane and carbon dioxide in a radio-frequency discharge, Ind. Eng. Chem. Res. 38 (1999) 2540–2547.

[7] Y. Wen, X. Jiang, Decomposition of CO_2 using pulsed corona discharges combined with catalyst, Environ. Sci. Technol. 21 (2001) 665–678.

[8] I. Maezono, J.-S. Chang, Reduction of CO_2 from combustion gases by DC corona torches, IEEE Trans. Ind. Appl. 26 (1990) 651–655.

[9] R. Li, Y. Yamaguchi, S. Yin., Q. Tang, T. Sato, Influence of dielectric barrier materials to the behavior of dielectric discharge plasma for CO_2 decomposition, Solid State Ionics 172 (2004) 235–238.

[10] J.-Y. Wang, G.-G. Xia, A. Huang, S.L. Suib, Y. Hayashi, H. Matsumoto, CO_2 decomposition using glow discharge plasmas, J. Catal. 185 (1999) 152–159.

[11] R.G. Buser, J.J. Sullovan, Intial process in CO_2 glow discharges, J. Appl. Phys. 41 (2) (1970) 472–479.

[12] A. Kobayashi, K. Osaki, C. Yamabe, Treatment of CO_2 gas by high-energy type plasma, Vacuum 65 (2002) 475–479.

[13] A. Fridman, S. Nester, L.A. Kennedy, A. Saveliev, O.M. Yardimci, Gliding arc gas discharge, Prog. Energy Combust. Sci. 25 (1999) 211.

[14] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Kinetic modeling of plasma methane conversion using gliding arc plasma, J. Nat. Gas Chem. 14 (2005) 13–21.

[15] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Effect of additive gases on methane conversion using gliding arc discharge, Energy 31 (2006) 2650–2659.

[16] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Gliding arc processing for decomposition of chloroform, Toxicol. Environ. Chem. 87 (2005) 509–519.

[17] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Treatment of dichloromethane using gliding arc plasma, Intl. J. Green Energy 3 (2006) 309–321.

[18] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Decomposition of CCl_4 and $CHCl_3$ on gliding arc plasma, J. Environ. Sci. 14 (2006) 81–88.

[19] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Treatment of CCl_4 and $CHCl_3$ emission in a gliding-arc plasma, Plasma Devices Oper. 14 (2006) 1–14.

[20] B. Eliasson, Nonequilibrium volume plasma chemical processing, IEEE Trans. Plasma Sci. 19 (1991) 1063–1077.

[21] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Conversion of CO_2 by gliding arc plasma, Environ. Eng. Sci. 23 (2006) 1033–1043.

[22] A. Indarto, J.W. Choi, H. Lee, H.K. Song, N. Coowanitwong, Discharge characteristic of a gliding-arc plasma in chlorinated methanes diluted in atmospheric air, Plasma Devices Oper. 14 (2006) 15–26.

[23] S.Y. Savinov, H. Lee, H.K. Song, B.-K. Na, The effect of vibrational of molecules of plasmachemical reaction involving methane and nitrogen, Plasma Chem. Plasma Process 23 (2003) 159–173.

[24] M.A. Lieberman, A.J. Lichtenberg, Principles of Plasma Discharges and Material Processing, first ed., John Wiley & Sons, New York, 1994.

[25] A. Goldman, J. Amouroux, Plasma chemistry, in: E.E. Kunhardt, L.H. Luessen (Eds.), Proc. Electrical Break and Discharges in Gases, Plenum Press, New York, 1981.

[26] H.R. Snyder, Effect of air and oxygen content on the dielectric barrier discharge decomposition of chlorobenzene, IEEE Trans. Plasma Sci. 26 (1998) 1695–1699.

[27] E. Jamshidi, The effect of a small amount of O_2 on vibrational excitation of N_2, J. Photochem. 9 (1978) 1–9.

[28] S.L. Suib, S.L. Brock, M. Marquez, J. Luo, H. Matsumoto, Y. Hayashir, Efficient catalytic plasma activation of CO_2, NO, and H_2O, J. Phys. Chem. B 102 (1998) 9661–9666.

[29] M. Anpo, K. Chiba, Photocatalytic reduction of CO_2 on anchored titanium oxide catalyst, J. Mol. Catal. 74 (1992) 207.

[30] R. Li, Y. Yamaguchi, S. Yin, Q. Tang, T. Sato, Influence of dielectric barrier materials to the behavior of dielectric barrier discharge plasma for CO_2 decomposition, Solid State Ionics 172 (2004) 235–238.

[31] L.T. Hsieh, W.J. Lee, C.T. Li, C.Y. Chen, Y.F. Wang, M.B. Chang, Decomposition of carbon dioxide in the RF plasma environment, J. Chem. Technol. Biotechnol. 73 (1998) 432–442.