

Comparison of different applied voltage waveforms on CO₂ reforming of CH₄ in an atmospheric plasma system

Duc Ba Nguyen and Won Gyu Lee[†]

Department of Chemical Engineering, Kangwon National University, Chuncheon-si, Kangwon-do 200-701, Korea

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Abstract—Sinusoidal and pulse waveforms of applied voltage were employed for CO₂ reforming of CH₄ to syngas in an atmospheric dielectric barrier discharge reactor. The discharge power of a pulse waveform was higher than that of sinusoidal waveform at the same applied voltage. The plasma reaction by a pulse waveform enhanced the conversion of CO₂ and CH₄ and the selectivity of H₂ and CO. It was confirmed that CO₂ reforming of CH₄ can be improved by the adaption of pulse-type power supply in a dielectric barrier discharge reactor immersed in an electrically insulating oil bath.

Keywords: Syngas, Dielectric Barrier Discharge, Atmospheric Plasma, Sinusoidal, Pulse

INTRODUCTION

CO₂ reforming of CH₄ to syngas has been the subject of great interest because two greenhouse gases are consumed and several valuable products can be produced. The products, such as ammonia, methanol, acetic acid, dimethyl ether, synthetic gasoline, and so on, can be used as the basic materials for other chemical reactions [1]. Recently and traditionally, a catalytic method [2,3], a plasma method [4-6] and plasma-catalyst method [7,8] have been employed for the reaction of CO₂ reforming of CH₄.

Reaction with a catalyst is still considered an attractive method, but the high temperature operation required for this method increases its cost. Also, the continuous formation and deposition of carbon black on the catalyst surface leads to the deactivation of the catalyst, which is the main disadvantage of this method [9,10]. As an effective approach, a plasma or plasma-catalyst method was suggested as a dry method of reforming methane, which could reduce the deposition of carbon black on the catalyst surface or electrode [11]. Several plasma systems have been employed for CO₂ reforming of CH₄, such as thermal plasma [4], corona discharge [12,13], arc discharge [5] and dielectric barrier discharge (DBD) [14-16]. Among the plasma systems, reaction by DBD has produced a relatively low degree of conversion of feed gases and selectivity of products. Therefore, many groups have researched ways to improve the efficiency of reaction by DBD [17-22]. Several research groups presented that CO₂-CH₄ reforming could be improved by a pulse-type power supply [23-27]. However, the previous comparison reports of waveforms on the reaction have performed without any concerns about energy efficiency, reaction time and reaction temperature [24-27]. In addition, their DBD reactors were directly exposed in the air, which could decrease the energy efficiency of waveforms [28]. Song et al. [26] reported that the reaction by a DBD

reactor was enhanced using a pulsed plasma, while the pulse width was not effective to enhance the conversion of reactants.

In this study, CO₂ reforming of CH₄ to syngas was performed by an atmospheric dielectric barrier discharge reactor immersed in an electrically insulating oil bath. For comparison of the effects of waveforms of applied voltage on the reaction, two kinds of waveforms, sinusoidal and pulse, were supplied to the plasma reactor for CO₂ reforming of CH₄. Several parameters, such as reaction time and applied voltage, were evaluated for the conversion of reactants, the selectivity of products, and the energy efficiency for both waveforms of applied voltage.

EXPERIMENTAL

A schematic diagram of experimental setup is shown in Fig. 1. The reactor had an inner stainless steel stick as the power electrode

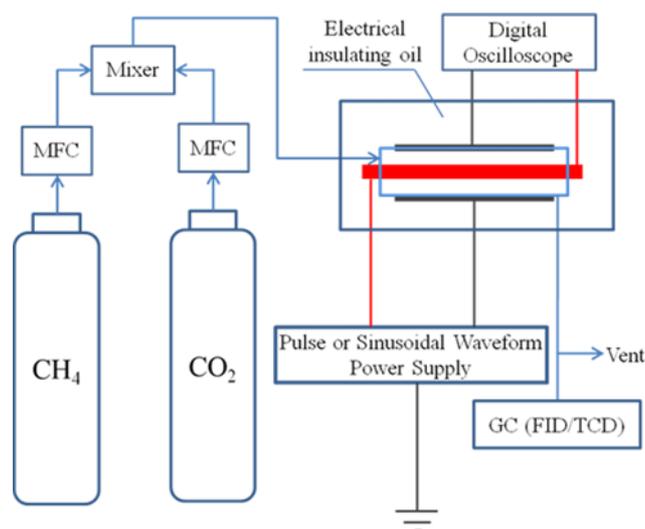


Fig. 1. Schematic diagram of the experimental setup.

[†]To whom correspondence should be addressed.

E-mail: wglee@kangwon.ac.kr

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which was 15 mm in diameter. The power electrode was placed inside a quartz tube as a dielectric barrier. Its outer diameter was 20 mm, and its thickness was 1.5 mm. Therefore, the gap between the outer surface of the power electrode and the inner surface of quartz tube was fixed at 1.0 mm. Copper foil was wrapped around the quartz tube as a ground electrode, and its length was 200 mm. Thus, the discharge volume was about 10 ml. The coaxial dielectric barrier discharge reactor was immersed in an electrically insulating oil bath (transformed oil was provided by Michang Oil, KSC2301). The bath volume filled with oil was about 4,000 ml, which could fully cover all of parts of reactor with oil.

The sinusoidal waveform was provided by AC power supply from Uion Co., while the pulse waveform was provided by AC pulse power supply from AP Plasma Co. The power supplies had some common electrical capacities such as a voltage up to 30 kV (peak-to-peak), a supply power of 2 kW, and a fixed frequency of 30 kHz. The input of the AC pulse power supply (pulse) was controlled by manual adjustment of the quantity of applied voltage. The power waveforms were recorded by an oscilloscope (Tektronix 2012B). Fig. 2 shows typical voltage, current, and discharge power waveforms generated during the process operation under the following process conditions: a total flow rate of 80 ml/min with CH₄/CO₂=1/1, an applied voltage of 7 kV, and frequency of 30 kHz. In the case of the sinusoidal waveform, the maximum current and delivered power was about 0.5 A and 500 W (Fig. 2(a)), while in the case of the pulse waveform, it was 1.5 A and 4,000 W (Fig. 2(b)), respectively. The pulse width was about 5.0 μs. Discharge power is calculated from the integration of current and voltage (1). Energy con-

version efficiency (2) and specific energy products (3) are defined as follows [6]:

Discharge power (P),

$$P(w) = \int_0^T U(t)I(t)dt \quad (1)$$

Energy conversion efficiency (ECE),

$$ECE\left(\frac{\text{kJ}}{\text{mol}}\right) = \frac{P\left(\frac{\text{kJ}}{\text{s}}\right)}{[\text{CH}_4 + \text{CO}_2]_{\text{converted}}\left(\frac{\text{mol}}{\text{s}}\right)} \quad (2)$$

Specific energy (SE),

$$SE\left(\frac{\text{kJ}}{\text{mol}}\right) = \frac{P\left(\frac{\text{kJ}}{\text{s}}\right)}{[\text{CO} + \text{H}_2]_{\text{produced}}\left(\frac{\text{mol}}{\text{s}}\right)} \quad (3)$$

All of the experiments were performed at ambient atmospheric pressure. The volume of gas products was measured by a soap-bubble flow meter. The composition of the products was analyzed by gas chromatography (GC, Younglin, YL6100GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) using CarboxenTM 1010 PLOT capillary column and Ar carrier gas. According to the analysis of the products, the overall conversions and selectivity can be defined as follows:

$$C_{\text{CH}_4}(\%) = \frac{\text{moles of CH}_4 \text{ converted (mol)}}{\text{moles of CH}_4 \text{ introduced (mol)}} \quad (4)$$

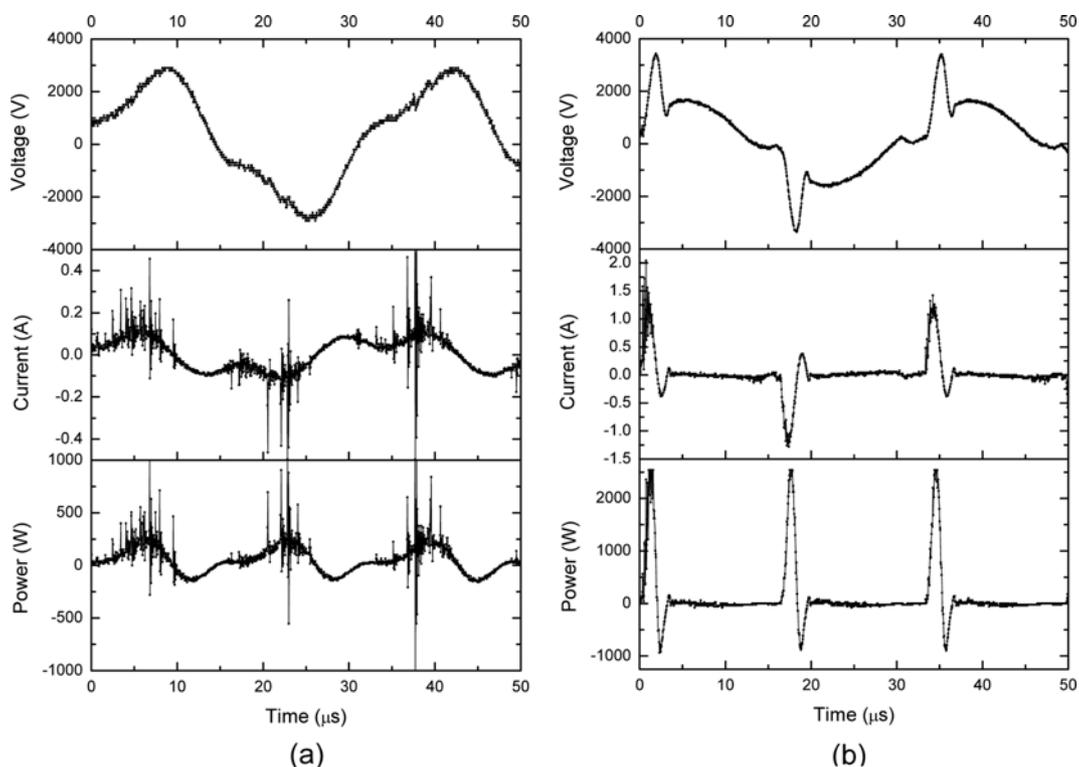


Fig. 2. Typical signal of voltage, current, and discharge power. (a) AC power supply and (b) AC pulse power supply with the process condition of a total flow rate=80 ml/min, a CH₄/CO₂=1 : 1 ratio of feed gases, and an applied voltage=7 kV).

$$C_{CO_2}(\%) = \frac{\text{moles of } CO_2 \text{ converted (mol)}}{\text{moles of } CO_2 \text{ introduced (mol)}} \quad (5)$$

$$S_{H_2}(\%) = \frac{\text{moles of } H_2 \text{ produced (mol)}}{2 \text{ moles of } CH_4 \text{ converted (mol)}} \quad (6)$$

$$S_{CO}(\%) = \frac{\text{moles of } CO \text{ produced (mol)}}{\text{moles of } (CH_4 + CO_2) \text{ converted (mol)}} \quad (7)$$

$$S_{\text{by-products}}(\%) = \frac{\text{moles of by-products produced (mol)}}{\text{moles of } (CH_4 + CO_2) \text{ converted (mol)}} \quad (8)$$

where by-product are hydrocarbons (C_xH_y , $x \geq 2$).

RESULTS AND DISCUSSION

1. Effect of Waveform of Applied Voltage on the Discharge Power and Energy Yield

An applied voltage is usually used to ignite and sustain glow discharge, and the degree of plasma reaction such as the conversion of feed gases and the selectivity of products depends on the level

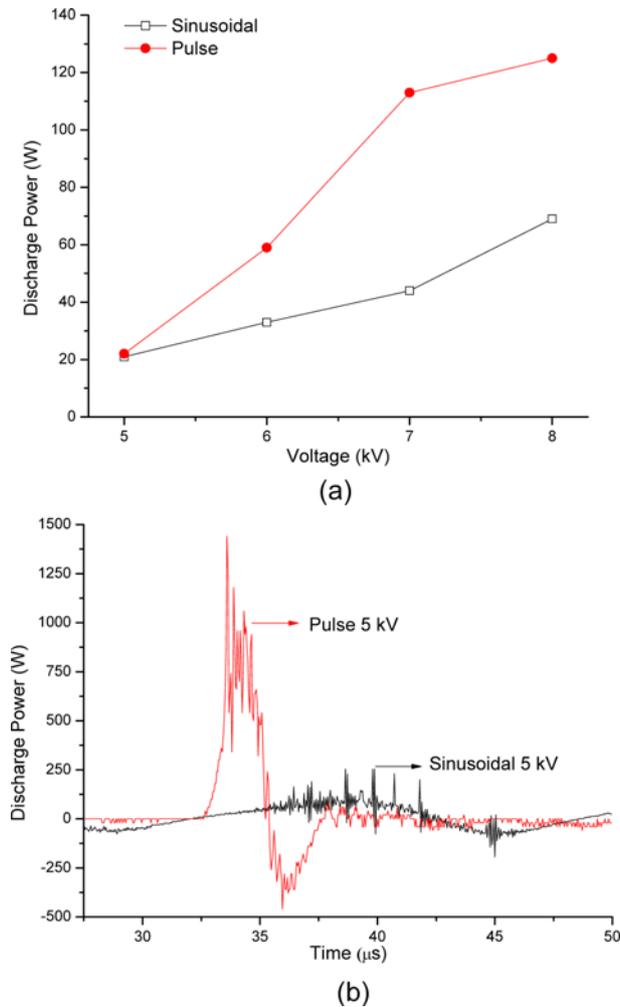


Fig. 3. (a) Comparison of discharge power delivered with different waveform of applied voltage and (b) the generation of discharge power at an applied voltage of 5 kV (total flow rate=80 ml/min; CH_4/CO_2 in feed=1 : 1).

of applied voltage [29]. The effect of applied voltage on the discharge power is shown in Fig. 3(a). The discharge power of sinusoidal waveform increased from 21 W to 69 W in the range from 5 kV to 8 kV. In the case of the pulse waveform, the discharge power rapidly increased from 21 W to 125 W in the same applied voltage range. The results show that the power delivered into the plasma reaction with a pulse waveform was superior to that with a sinusoidal at the same level of applied voltage. The integration of instantaneous power was about 21 W at 5 kV for both waveforms as seen in Fig. 3(b). As the applied voltage was increased, the integration of instantaneous pulse power was higher than that of sinusoidal power under the same condition when the applied voltage was in the range from 6 to 8 kV. This indicates that the energy input of the pulse-type waveform into the discharge zone is higher than that of sinusoidal-type waveform at an applied voltage over 5 kV.

In the micro-discharge, the current amplitude of pulse waveform was higher than that of sinusoidal waveform at the same condition as shown in Fig. 2. In detail, the current amplitude of sinusoidal waveform was about 0.5 A, while that of pulse waveform of 1.5 A. The results indicate that the electrical conductivity of plasma gas in pulse waveform was higher than that of sinusoidal waveform at the same condition. It means that the density of electrons, ions, excited species, and radicals in pulse waveform process was higher than those in sinusoidal waveform process. This reveals that a pulse waveform could have more chemical activity than a sinusoidal waveform at the same plasma condition.

The energy conversion efficiency (ECE) and specific energy (SE) of the reactors were considered to compare the energy yield of voltage waveforms as shown in Fig. 4. The reactions were performed with variation of the applied voltage and its waveform with fixed parameters of a total flow rate=80 ml/min and a CH_4/CO_2 ratio=1/1. ECE and SE have a tendency to increase when applied voltage increases from 5 kV to 8 kV regardless of the type of voltage waveform, showing that the energy efficiency for the reforming reaction becomes lower as the applied voltage increases. In detail, about 60% of input power into discharge zone usually uses for the barrier heating in a dielectric barrier discharge reactor [30,31].

A comparison of the results shows that the ECE and SE of the

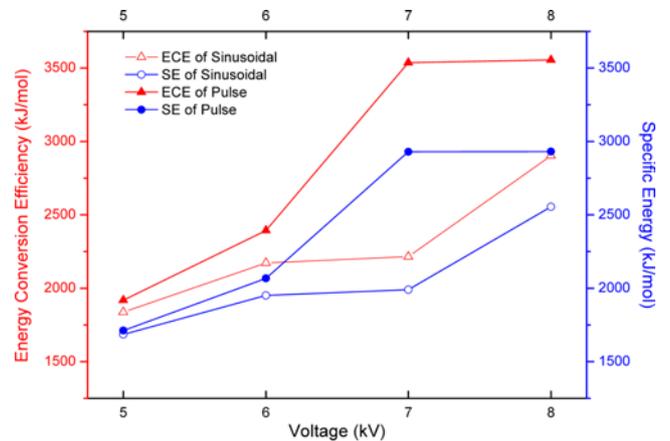


Fig. 4. Energy conversion efficiency (ECE) and specific energy (SE) (total flow rate=80 ml/min; CH_4/CO_2 in feed=1 : 1).

sinusoidal waveform were lower to those of the pulse waveform at the same condition, which means that energy consumption of sinusoidal waveform is lower than that of pulse waveform for the same reactant conversion or products formation at the same condition. As well, an applied sinusoidal waveform is more energy efficient for CO₂ reforming of CH₄ for syngas. Thus, the input energy yield in the discharge of sinusoidal power was higher than that of pulse power at the same applied voltage. The maximum ECE and SE in our experiment were obtained at 3,598 kJ/mol and 2,885 kJ/mol, respectively, in the applied voltage with pulse waveform of 8 kV.

For comparison our system with several systems in dry reforming of methane, an energy efficiency could be considered. Energy efficiency can be described as the conversion of CH₄ or CO₂ per input power, which is equal to 1/ECE (mmol/kJ). The minimum energy efficiency was 0.281 mmol/kJ at an applied voltage of 8 kV with pulse waveform. Energy efficiency in our experiment was lower than those of thermal plasma and plasma jet [32,33]. However, it was slightly higher or comparable than energy efficiency for CH₄ and CO₂ conversion by several dielectric barrier discharge systems [15,34,35].

Snoeck et al. [36] indicated that the consumption of energy was at least 330 MJ for the reaction between 1 kmol CH₄ and 1 kmol CO₂ in the industrial scale the dry reforming of methane. The process performed most efficient at 700 °C; the conversion of CH₄ and CO₂ was obtained at 72% and 82%, respectively. Therefore, energy efficiency of the process is 4.667 mmol·kJ⁻¹. It was 16.6 times compared with the energy efficiency obtained in our experiment at applied voltage of 8 kV with pulse waveform.

2. Effect of Reaction Time on the Reaction

Reaction time is also an important factor because it has a strong influence on the degree of plasma reaction and the reactor temperature [23]. The effect of reaction time on the reaction was investigated under the process condition of a total flow rate of 80 ml/min, a CH₄/CO₂=1/1 ratio of feed gases, and an applied voltage of 7 kV. Because the reactor was immersed in the oil bath, the reactor temperature can be considered as the oil temperature in this experiment. The oil temperature was monitored according to the

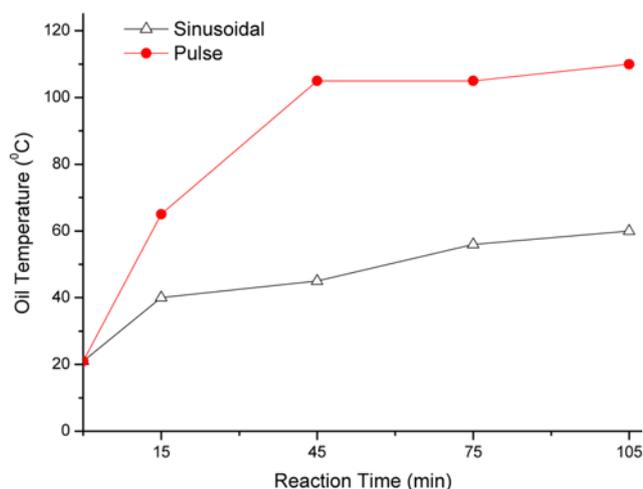


Fig. 5. Oil temperature vs. reaction time (total flow rate=80 ml/min; CH₄/CO₂ in feed=1 : 1; applied voltage=7 kV).

reaction time as shown in Fig. 5. During the reaction up to 105 min, the oil temperature increased regardless of the type of applied waveforms. The temperature with the application of sinusoidal waveform increased from 21 to 65 °C, while in the case of pulse waveform, the temperature increased from 21 to 110 °C under the same process conditions. These results suggest that the delivered discharge power with the pulse waveform (113 W) was higher than that with the sinusoidal waveform (44 W). According to the previous research results [30,31], the energy for heating a DBD reactor was sourced from about 60% of discharge power. Therefore, the energy transfer in the discharge causes the increase of system temperature. Thus, the amount of available discharge power with the pulse waveform for heating the reactor system was larger than that with the sinusoidal waveform.

The conversion of CH₄ and CO₂ and the selectivity of products were not influenced by the reaction time or the reactor temperature for both types of waveform as shown in Fig. 6. According to a previous report [23], the degree of plasma reaction was strongly influenced by the reactor temperature for CO₂ reforming of CH₄,

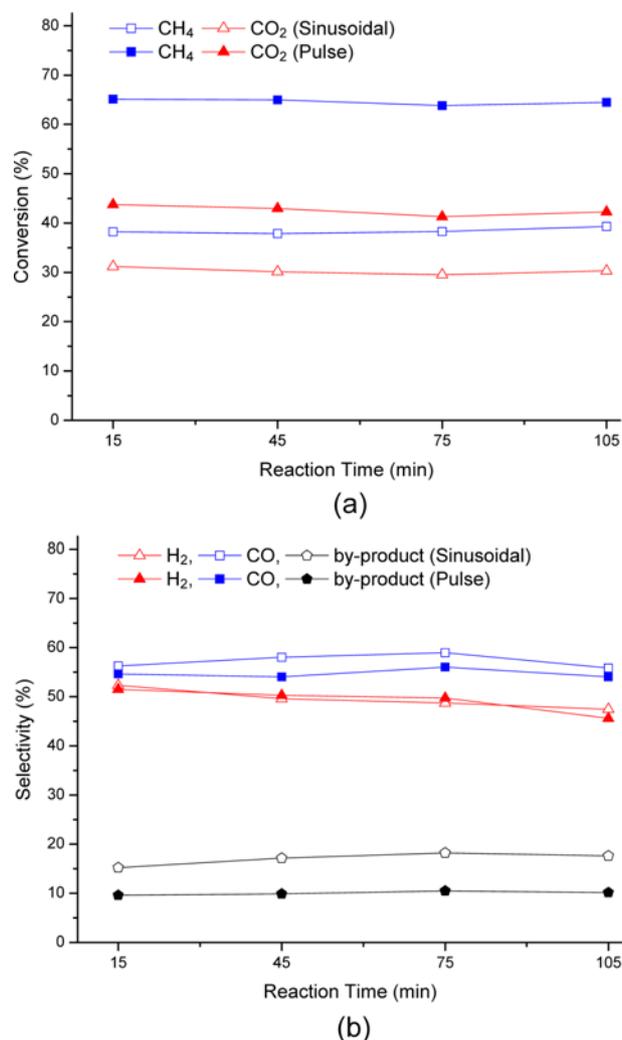


Fig. 6. Effect of reaction time on (a) conversion of CH₄ and CO₂, (b) selectivity of H₂, CO and by-product (total flow rate=80 ml/min; CH₄/CO₂ in feed=1 : 1; applied voltage=7 kV).

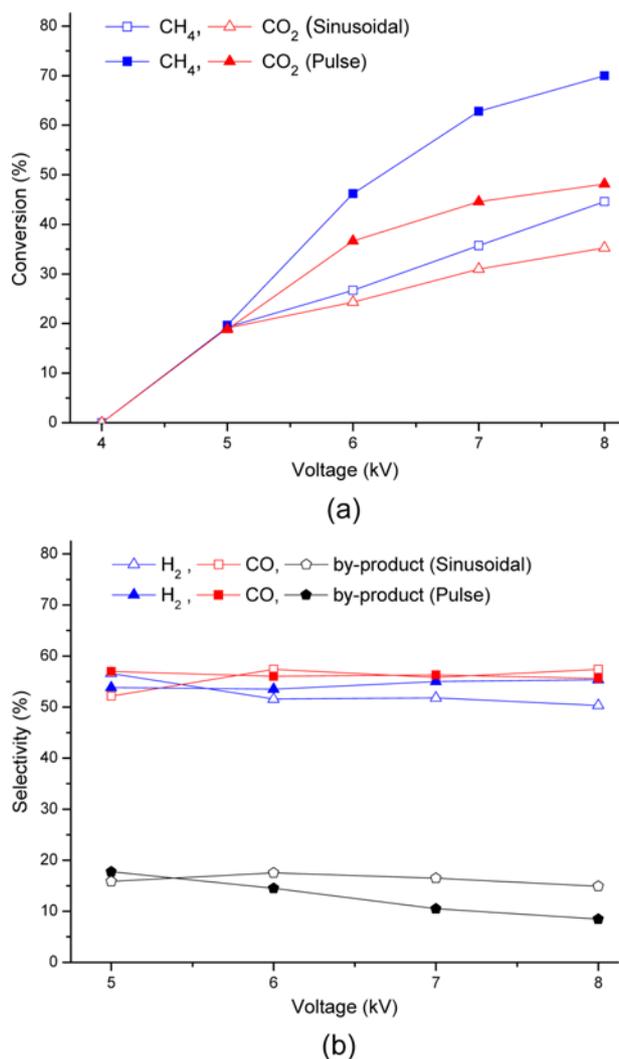


Fig. 7. Effect of applied voltage on (a) conversion of CH₄ and CO₂, (b) selectivity of H₂, CO and by-product (total flow rate=80 ml/min; CH₄/CO₂ in feed=1).

when the temperature was higher than 200 °C. Under this experimental condition, because the maximum raising temperature of oil was about 110 °C, which was lower than the influential temperature of over 200 °C, the values of conversion and selectivity were not significantly changed with the reaction time or the reactor temperature under the given process conditions.

3. Effect of Applied Voltage on the Reaction

The influence of applied voltage on the reaction is shown in Fig. 7. The conversion of CH₄ and CO₂ was almost 0% at 4.0 kV due to the unavailability of plasma ignition. Through visual inspection, we confirmed that the plasma did not ignite below an applied voltage of 5 kV (21 W). However, the conversion of CH₄ and CO₂ was significant at an applied voltage of 5.0 kV with an energy input of about 21 W for both waveforms. The results indicate that the energy input to the discharge yields energetic electrons in the range of 1-10 eV, which is enough to dissociate CO₂ and CH₄ molecules with the dissociation energies of 5.5 and 4.5 eV, respectively [29]. High energy electrons could be colliding and dissociate reactant mole-

cules to formation of radicals, ions and products R (1)-R (9) [29,36].



At an applied voltage of 5 kV, the conversions of CH₄ and CO₂ of pulse waveform were the same than that of sinusoidal waveform. The conversion of CH₄ and CO₂ increased with the increase of applied voltage from 5 kV to 8 kV. Electron impact reactions are primary reactions for conversion of reactants in the non-thermal plasma for dry reforming [36]. Therefore, the conversions of reactants depend on the energy of electrons and electron density. Energy of electrons and electron density increased by increasing discharge power. Consequently, the conversions of reactants increase with increasing applied voltage for both waveforms. However, the conversions of reactants in pulse waveform were higher than those in sinusoidal waveform under the condition of applied voltage above 5 kV at the same plasma condition.

In addition, the conversion of CH₄ was higher than the conversion of CO₂ for both powers supplies at an applied voltage above 5 kV. The results could be archived from the fact that the energy of electron impact dissociation for CH₄ is lower than that for CO₂ [35-37]. In detail, more conversion of CH₄ may be performed by electron impact dissociate reactions exist of R (1)-R (5). The maximum conversion levels of CH₄ and CO₂ were obtained at 70.0% and 48.2%, respectively, with the pulse-type waveform at the applied voltage of 8 kV.

The selectivity of H₂ and CO did not change significantly for either waveform as shown in Fig. 7(b). The selectivity of H₂ and CO showed similar values of around 55%. Whereas, by-product selectivity decreased with the increased applied voltage for both waveforms. Selectivity of by-product with the pulse waveform was similar to by-product selectivity with the sinusoidal waveform at 5 kV. By-product including C₂H₆ molecules could be formed by recombination of CH₃ radicals as shown in reaction R (10). Ionization degree and meta-stables increased at high-applied voltage due to reducing formation of C₂H₆ by the reaction R (10). Moreover, C₂H₆ could be ionized and interacted with CO₂ formed to CO and H₂ stable molecules at high-applied voltage [15]. Therefore, the selectivity of by-product decreased by applied voltage increased for both waveforms.

CONCLUSION

CO₂ reforming of CH₄ to syngas by a coaxial dielectric barrier

discharge immersed in an electrically insulating oil bath was performed under two kinds of applied voltage: pulse-type and sinusoidal-type waveform. The reactor temperature equal to the oil bath was reached to 110 °C from room temperature after the reaction time of 105 min when the pulse waveform was delivered. However, the performance of the plasma reaction, in terms of the conversion of feed gas and product selectivity, did not change significantly under the slightly heated condition. The ECE and SE with sinusoidal waveform were lower than those with pulse waveform at the same applied voltage. This indicates that a sinusoidal waveform is more energy effective for CO₂ reforming of CH₄ for syngas. However, the delivered sinusoidal power at the applied voltage was always lower than the delivered pulse power; thus, the reactant conversion and product selectivity with the pulse waveform were higher than those with sinusoidal waveform under the same process conditions.

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REFERENCES

- J. R. Rostrup-Nielsen, *Catal. Today*, **63**, 159 (2000).
- M. C. J. Bradford and M. A. Vannice, *Catal. Rev.*, **41**, 1 (1999).
- R. Martinez, E. Romero, C. Guimon and R. Bilbao, *Appl. Catal. A: Gen.*, **274**, 139 (2004).
- X. Tao, M. Bai, Q. Wu, Z. Huang, Y. Yin and X. Dai, *Int. J. Hydrog. Energy*, **34**, 9373 (2009).
- A. Indarto, J. Choi, H. Lee and H. Song, *Energy*, **31**, 2986 (2006).
- X. Tao, M. Bai, X. Li, H. Long, S. Shang, Y. Yin and X. Dai, *Prog. Energy Combust. Sci.*, **37**, 113 (2011).
- H. Long, S. Shang, X. Tao, Y. Yin and X. Dai, *Int. J. Hydrog. Energy*, **33**, 5510 (2008).
- X. Tu, H. J. Gallon, M. V. Twigg, P. A. Gorry and J. C. Whitehead, *J. Phys. D: Appl. Phys.*, **44**, 274007 (2011).
- E. Promaros, S. Assabumrungrat, N. Laosiripojana, P. Prasertthadam, T. Tagawa and S. Goto, *Korean J. Chem. Eng.*, **24**, 44 (2007).
- A. E. Castro Luna and M. E. Iriarte, *Appl. Catal. A: Gen.*, **343**, 10 (2008).
- H. J. Gallon, X. Tu, M. V. Twigg and J. C. Whitehead, *Appl. Catal. B: Environ.*, **106**, 616 (2011).
- H. Le, L. L. Lobban and R. G. Mallinson, *Catal. Today*, **89**, 15 (2004).
- D. Liu, R. Lau, A. Borgna and Y. Yang, *Appl. Catal. A: Gen.*, **358**, 110 (2009).
- B.-B. Hwang, Y.-K. Yeo and B.-K. Na, *Korean J. Chem. Eng.*, **20**, 631 (2003).
- Q. Wang, B.-H. Yan, Y. Jin and Y. Cheng, *Plasma Chem. Plasma Process.*, **29**, 217 (2009).
- T. K. Kim and W. G. Lee, *J. Ind. Eng. Chem.*, **18**, 1710 (2012).
- X. Chen, M. Marquez, J. Rozak, C. Marun, J. Luo, S. L. Suib, Y. Hayashi and H. Matsumoto, *J. Catal.*, **178**, 372 (1998).
- Y. Li, G.-h. Xu, C.-j. Liu, B. Eliasson and B.-z. Xue, *Energy Fuels*, **15**, 299 (2001).
- S. Yao, A. Nakayama and E. Suzuki, *AIChE J.*, **47**, 419 (2001).
- S. L. Brock, T. Shimojo, S. L. Suib, Y. Hayashi and H. Matsumoto, *Res. Chem. Intermed.*, **28**, 13 (2002).
- B. Sarmiento, J. J. Brey, I. G. Viera, A. R. Gonzalez-Elipe, J. Cotrino and V. J. Rico, *J. Power Sources*, **169**, 140 (2007).
- V. J. Rico, J. L. Hueso, J. Cotrino and A. R. Gonzalez-Elipe, *J. Phys. Chem. A*, **114**, 4009 (2010).
- S. Yao, A. Nakayama and E. Suzuki, *AIChE J.*, **47**, 413 (2001).
- V. Goujard, J. M. Tatibouet and C. Batiot-Dupeyrat, *IEEE Trans. Plasma Sci.*, **37**, 2342 (2009).
- N. Benard and E. Moreau, *Appl. Phys. Lett.*, **100**, 193503 (2012).
- H. Song, H. Lee, J.-W. Choi and B.-k. Na, *Plasma Chem. Plasma Process.*, **24**, 57 (2004).
- H. Lee, C.-H. Lee, J.-W. Choi and H. K. Song, *Energy Fuels*, **21**, 23 (2007).
- D. B. Nguyen and W. G. Lee, *J. Ind. Eng. Chem.*, **20**, 972 (2014).
- L. M. Zhou, B. Xue, U. Kogelschatz and B. Eliasson, *Energy Fuels*, **12**, 1191 (1998).
- T. Hammer, T. Kappes and M. Baldauf, *Catal. Today*, **89**, 5 (2004).
- T. Nozaki, Y. Miyazaki, Y. Unno and K. Okazaki, *J. Phys. D: Appl. Phys.*, **34**, 3383 (2001).
- D. Li, X. Li, M. Bai, X. Tao, S. Shang, X. Dai and Y. Yin, *Int. J. Hydrog. Energy*, **34**, 308 (2009).
- X. M. Tao, F. W. Qi, Y. P. Yin and X. Y. Dai, *Int. J. Hydrog. Energy*, **33**, 1262 (2008).
- Y.-p. Zhang, Y. Li, Y. Wang, C.-j. Liu and B. Eliasson, *Fuel Process. Technol.*, **83**, 101 (2003).
- X. Tu and J. C. Whitehead, *Appl. Catal. B: Environ.*, **125**, 439 (2012).
- R. Snoeckx, R. Aerts, X. Tu and A. Bogaerts, *J. Phys. Chem. C*, **117**, 4957 (2013).
- H. J. Gallon, X. Tu and J. C. Whitehead, *Plasma Process. Polym.*, **9**, 90 (2012).