

# Reduction of carbon dioxide particles to carbon monoxide by nonthermal plasma

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## Abstract

Nonthermal plasma reduces carbon dioxide to carbon monoxide, which can be converted into fuels and organic compounds, and is used as a raw material for gas synthesis. However, the energy efficiency is currently too low for practical use, and innovative ideas are required. This study proposes a CO<sub>2</sub> fuel conversion technology using solid CO<sub>2</sub> in a nonthermal plasma reactor. The advantages of using solid CO<sub>2</sub> are the suppression of the CO re-oxidation reaction at low temperatures and the improvement in energy efficiency at high CO<sub>2</sub> concentrations. In the experiment, the plasma reduction of gaseous and solid CO<sub>2</sub> is performed using a dielectric barrier discharge plasma reactor, and the conversion and energy efficiencies are compared. The concentration of generated CO is found to be dependent on the concentration of CO<sub>2</sub>. When nonthermal plasma is applied to solid CO<sub>2</sub>, Joule heating causes CO<sub>2</sub> sublimation, which reduces gaseous CO<sub>2</sub> to CO. The solid CO<sub>2</sub> in the plasma reactor increases the impedance and decreases the discharge power. The introduction of solid CO<sub>2</sub> upstream of the reactor increases the discharge power and improves the CO conversion efficiency. At a specific energy of 1.8 eV/molecule, the reduction of solid CO<sub>2</sub> increases the conversion efficiency from 1.4% to 1.8% and the energy efficiency from 2.3% to 2.7%, compared to the reduction of gaseous CO<sub>2</sub>.

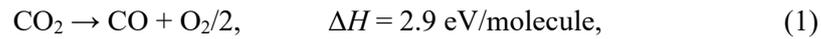
**Keywords:** Nonthermal plasma, carbon dioxide, carbon monoxide, solid-phase of CO<sub>2</sub>, dielectric barrier discharge.

## 1. Introduction

The concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere has increased significantly due to the burning of fossil fuels and deforestation. CO<sub>2</sub> is a greenhouse gas that absorbs heat radiated from the Earth's surface to outer space and radiates it back to the surface. As the concentration of CO<sub>2</sub> in the atmosphere increases, global warming progresses, causing serious damage to the global environment, such as increasing sea levels, unusual weather, and ecosystem destruction. Therefore, technologies for capturing and treating CO<sub>2</sub> have become increasingly important.

Carbon capture and storage (CCS) is a promising technology for reducing emissions and is projected to account for 14% of cumulative CO<sub>2</sub> emission reductions by 2050 [1]. CCS involves capturing and separating CO<sub>2</sub> from fossil fuel-fired power plants, transporting it to a designated storage site, and injecting it into a suitable carbon-bearing layer deep beneath the ocean. In the separation portion, CO<sub>2</sub> can be isolated using cryogenic separation, membrane separation, or sorbents such as chemical absorption and solid adsorption. Typical sorbents include molecular sieves, zeolites, calcium oxides, hydrotalcites, and lithium zirconate [2]. These methods achieve approximately 100% CO<sub>2</sub> concentration. However, the current adsorption technologies are expensive [3]. Therefore, there is a need for CO<sub>2</sub> treatment technologies that are both cost-effective and highly efficient to ensure sustainable CO<sub>2</sub> emission reduction.

By contrast, CO<sub>2</sub> conversion technology to carbon monoxide (CO) or C1 materials using metal catalysts or photocatalysts has also been proposed [4–9]. CO is converted to syngas when mixed with hydrogen (H<sub>2</sub>) and has been studied for use as a fuel in gas-turbine engines [10, 11]. In addition to catalytic technology, nonthermal plasma (NTP) is widely used for converting CO<sub>2</sub> to CO at atmospheric pressure and temperature [12–24]. CO<sub>2</sub> reduction is achieved by applying an NTP characterized by fast electrons and atmospheric discharge. In NTP-based technology, CO<sub>2</sub> is mainly reduced to CO via a plasma chemical reaction [25], as shown in (1)



where  $\Delta H$  is the enthalpy of the reaction. In addition, the following reactions (2) and (3) are the major reactions of  $\text{CO}_2$  reduction in the plasma reactor. However, these two reactions are considered negligible in this study due to the low power density of plasma generation [26].



where M is third body in the reaction process. One challenge of this technology is its energy efficiency. Ideally, this can be reduced to 2.9 eV/molecule; currently, more than twice the amount of energy must be invested. Identifying the source of  $\text{CO}_2$  is challenging. For example, flue gas from a thermal power plant has a  $\text{CO}_2$  concentration of approximately 10%, and more energy is required to increase this concentration from 10% to 100% to improve energy efficiency. This challenge is more significant for  $\text{CO}_2$  in air at 400–500 ppm. Our research group proposed a technology that simultaneously conducts  $\text{CO}_2$  adsorption/concentration and reduction with an NTP by combining an adsorbent with NTP [27–29]. Results of  $\text{CO}_2$  concentration and reduction in simulated combustion exhaust gas and air show relatively good results of  $\text{CO}_2$  conversion and energy efficiency of 21% and 13%, respectively; however, further improvement of energy efficiency is required for practical use.

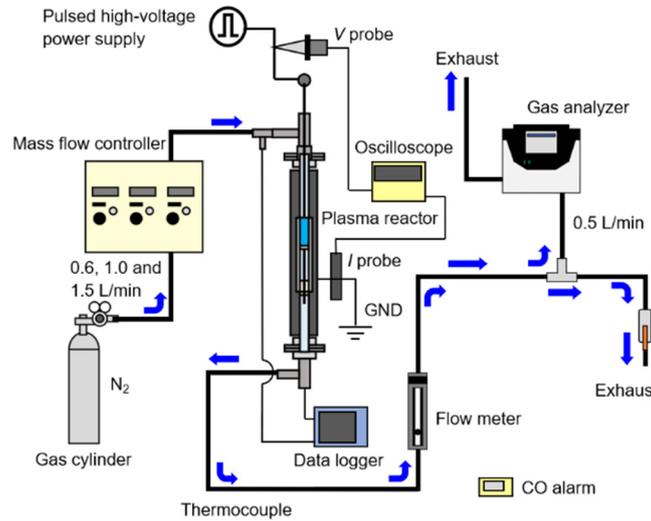
To improve the energy efficiency, Lu *et al.* [30] cooled plasma reactors. By cooling the plasma reactor temperature from 120 °C to 40 °C by water cooling, a 6% increase in CO conversion efficiency and 2% improvement in energy efficiency have been reported. Decreasing the temperature of the reaction region of the reactor suppresses the recombination reactions to  $\text{CO}_2$  and improves the effective utilization rate of the input energy in the reaction system. Berthelot and Bogaerts [26] modelled  $\text{CO}_2$  reduction using microwave plasma and the effects of pressure and temperature on energy efficiency.

Based on this background, this study performs NTP reduction on solid-phase  $\text{CO}_2$  particles called dry ice particles, considering that NTP treatment of  $\text{CO}_2$  at lower temperatures and higher densities may improve energy efficiency.  $\text{CO}_2$  separated and recovered from flue gas using adsorbents or membrane separation is generally transported and stored in a gaseous state for short-distance transportation or immediate use, whereas it is transported and stored in liquid and solid states for long-distance transportation or storage purposes.  $\text{CO}_2$  in the liquid state can be easily converted into solid  $\text{CO}_2$  through adiabatic expansion. Therefore, this study focuses on solid  $\text{CO}_2$ , which has a higher density than the gaseous state, and aims to verify the effectiveness of a  $\text{CO}_2$  reduction system using solid  $\text{CO}_2$  and evaluate the energy efficiency of the NTP reduction technology for solid  $\text{CO}_2$ .

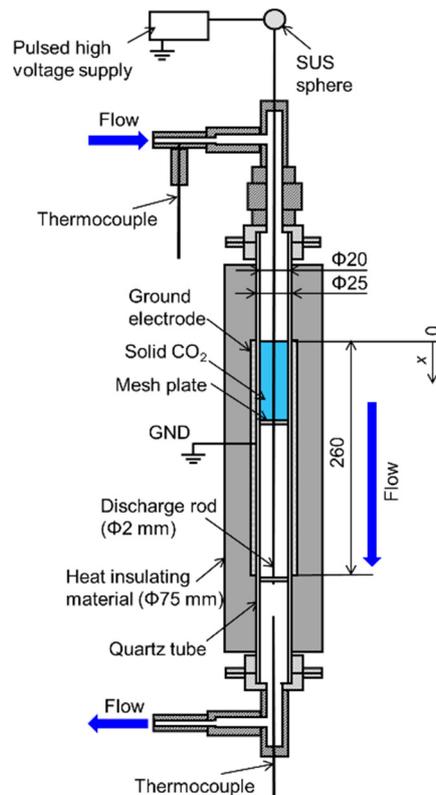
## 2. Experimental

Fig. 1 shows a schematic of the experimental setup for solid  $\text{CO}_2$  reduction using a dielectric barrier discharge plasma reactor. The experimental apparatus comprises an  $\text{N}_2$  cylinder, mass flow meter, plasma reactor, pulsed high-voltage power supply, oscilloscope, data logger, and gas analyzer. A mass-flow controller (SFC-281E, Hitachi Metals, Ltd., Japan) is used to adjust the flow rate of the  $\text{N}_2$  cylinder (purity = 99.995%).  $\text{N}_2$  gas flows from the top of the plasma reactor filled with solid  $\text{CO}_2$  particles, and the reactor is energized with a high voltage to generate NTP and reduce  $\text{CO}_2$  to CO. The treated gas flows from the bottom of the reactor, and the concentrations are measured using a  $\text{CO}_2$ , CO,  $\text{O}_2$ , NO, and  $\text{NO}_x$  analyzer (PG350, Horiba, Ltd., Japan;  $\text{CO}_2 < 20\%$ ,  $\text{CO} < 5000$  ppm,  $\text{O}_2 < 25\%$ ,  $\text{NO} < 2500$  ppm,  $\text{NO}_x < 2500$  ppm). Fig. 2 shows a detailed schematic of the plasma reactor. The plasma reactor comprises a discharge wire, quartz tube, grounding electrode, and an insulator. The quartz tube is a cylindrical tube with an inner diameter of 20 mm, outer diameter of 25 mm, a length of 646 mm, and a 0.05 mm thick ground electrode in a 260 mm longitudinal section (discharge area). The discharge wire is made of stainless steel with a diameter of 2.0 mm and is placed at the radial center of the quartz tube. An insulated gate bipolar transistor (IGBT) pulsed high-voltage power supply (PPCP Pulsar SHC-30/1000, Masuda Research Inc., Japan) is used as the plasma power supply, and a high voltage is applied to the discharge wire to generate NTP between the wire and ground electrode. The voltage applied to the reactor and discharge current are measured with an oscilloscope (DLM2054, Yokogawa Electric Co., Japan)

using a voltage probe (P6015A, conversion factor = 1 kV/V, Tektronix Inc.) and a current probe (P6021, conversion factor = 10 A/V, Tektronix Inc.). The discharge mode is a pulsed dielectric barrier discharge (DBD). Solid CO<sub>2</sub> is generated by the adiabatic expansion of CO<sub>2</sub> from a liquid CO<sub>2</sub> cylinder, and the mass is measured before filling part of the reactor. To generate solid CO<sub>2</sub>, silica gel is placed in the generation vessel to prevent coagulation and binding with moisture in the air, and the vessel is vacuumed after CO<sub>2</sub> purging to sufficiently remove moisture before generation. Fig. 3 shows a photograph of the solid CO<sub>2</sub> particles generated. The particles are irregularly shaped and range in diameter from 0.5 to 5.0 mm with an average particle size of approximately 1 mm.



**Fig. 1.** Schematic of experimental setup.



**Fig. 2.** Plasma reactor.

The experimental conditions are as follows: solid CO<sub>2</sub> is filled in the range of  $x = -100-0, 0-50, 0-100, 0-150$  mm, N<sub>2</sub> flow rate 0.6, 1.0, and 1.5 L min<sup>-1</sup>, voltage 20–26 kV, voltage frequency 210, 520, and 840 Hz. Here,  $x = 0$  indicates the upper end of the discharge region of the reactor, and minus indicates the upstream end of the reactor. The experiment is conducted until the solid CO<sub>2</sub> has completely sublimated and the gas concentration has reached a steady state to prevent excessive temperature increases in the reactor. This study includes a gaseous CO<sub>2</sub> reduction experiment for comparison. Gaseous CO<sub>2</sub> reduction experiments are performed using CO<sub>2</sub> and N<sub>2</sub> cylinders with a mixture of CO<sub>2</sub> = 20% and N<sub>2</sub> = 80% by adjusting the flow rate using a mass flow meter, changing the applied pulse frequency to 210, 520, and 840 Hz, and discharging it for 10 min. The CO conversion efficiency  $\alpha$  and energy efficiency  $\eta$  are used to evaluate the experiment.  $\alpha$  represents the fraction of CO<sub>2</sub> molecules that are reduced to CO and is determined by Equation (4) from CO<sub>2</sub> and CO concentration, while energy efficiency is determined by Equation (5).

$$\alpha = \text{CO} / (\text{CO} + \text{CO}_2) \times 100 \quad (4)$$

$$\eta = \alpha \times \frac{\Delta H}{E_v} \quad (5)$$

Here,  $E_v$  is the specific energy of the plasma obtained from the discharge power  $P$  (W) and gas flow rate  $Q$  (L min<sup>-1</sup>) using the following equation:

$$E_v = \left( \frac{P}{1.602 \times 10^{-19}} \right) / \left( \frac{\text{CO}_2 \times Q}{60} \times 22.4 \times 6.02 \times 10^{23} \times \frac{273.15}{T} \right) \quad (6)$$

where  $T$  (K) is room temperature.

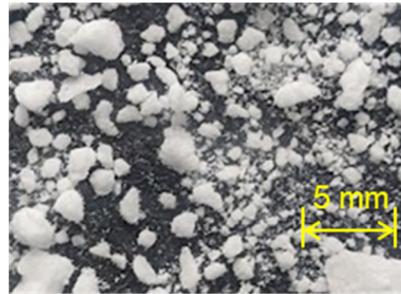


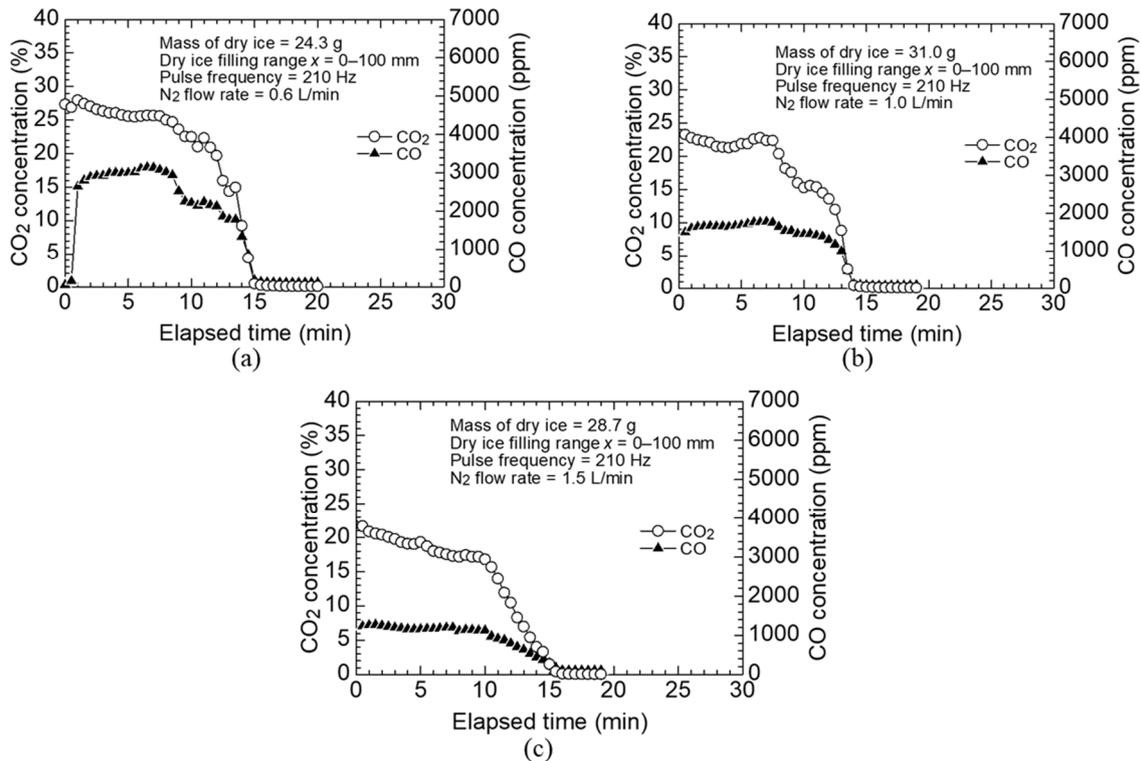
Fig. 3. Photograph of solid CO<sub>2</sub> particles.

### 3. Results and discussion

#### 3.1 Effect of N<sub>2</sub> flow rate on CO and CO<sub>2</sub> concentration

Figs. 4 (a)–(c) show the experimental results of the time-dependent CO<sub>2</sub> and CO concentrations for a solid CO<sub>2</sub> filling range of  $x = 0-100$  mm, pulse frequency of 210 Hz, and N<sub>2</sub> flow rates of (a) 0.6 L min<sup>-1</sup>, (b) 1.0, and (c) 1.5 L min<sup>-1</sup>. As shown in Fig. 4 (a), the initial concentration of CO<sub>2</sub> is 26%, which is caused by the sublimation of solid-phase CO<sub>2</sub> to gaseous CO<sub>2</sub> owing to the forced thermal convection caused by the N<sub>2</sub> flow and Joule heating caused by the discharge. CO<sub>2</sub> decreases with time, and no CO<sub>2</sub> is detected after 15 min. CO is generated immediately after the start of the discharge, increasing to a maximum of 3147 ppm at 7 min and decreasing as CO<sub>2</sub> decreases. The CO<sub>2</sub> flow rate, calculated from the N<sub>2</sub> flow rate and CO and CO<sub>2</sub> concentrations, gradually decreases from 0.23 L min<sup>-1</sup> at 1 min to 0.21 L min<sup>-1</sup> at 7 min. As shown in Fig. 4 (b), the initial concentration of CO<sub>2</sub> is 24% and CO<sub>2</sub> decreases with time, and no CO<sub>2</sub> is detected after 15 min. CO is generated immediately after the start of the discharge, increasing to a maximum of 1791 ppm at 7 min,

and decreasing as CO<sub>2</sub> decreases. The CO<sub>2</sub> flow rate gradually decreases from 0.30 L min<sup>-1</sup> at 1 min to 0.29 L min<sup>-1</sup> at 7 min. As shown in Fig. 4 (c), the initial concentration of CO<sub>2</sub> is 23%; CO<sub>2</sub> decreases with time, and no CO<sub>2</sub> is detected after 16 min. CO is generated immediately after the start of the discharge and increases to a maximum of 1273 ppm at 3 min, gradually decreasing by 100 ppm at 10 min, and then decreasing to zero after 10 min. The CO<sub>2</sub> flow rate gradually decreases from 0.46 L min<sup>-1</sup> at 1 min to 0.39 L min<sup>-1</sup> at 3 min and 0.31 L min<sup>-1</sup> at 10 min. The figures show that the CO concentration decreases as the N<sub>2</sub> flow rate increases. This is caused by a decrease in residence time. The residence times calculated from the mixed flow rate and the discharge region (0.08 L) when the CO concentration is at its maximum are 6.0, 3.8, and 2.6 s for N<sub>2</sub> flow rates of 0.6, 1.0, and 1.5 L min<sup>-1</sup>, respectively. This indicates that the CO concentration depends on the residence time. The time required for all solid CO<sub>2</sub> to sublimate is approximately 15 min in all cases, indicating that Joule heating, rather than forced thermal convection, is dominant for solid CO<sub>2</sub> sublimation.



**Fig. 4.** Time-dependent CO<sub>2</sub> and CO concentrations at  $f = 210$  Hz and  $x = 0$ –100 mm (a) N<sub>2</sub> = 1.0 L min<sup>-1</sup>, (b) N<sub>2</sub> = 1.0 L min<sup>-1</sup>, (c) N<sub>2</sub> = 1.0 L min<sup>-1</sup>.

Fig. 5 (a)–(c) show the discharge power during the experiment for a solid CO<sub>2</sub> filling range of  $x = 0$ –100 mm, a pulse frequency of 210 Hz, and N<sub>2</sub> flow rates of (a) 0.6 L min<sup>-1</sup>, (b) 1.0, and (c) 1.5 L min<sup>-1</sup>. As shown in Fig. 5 (a), at the beginning of the discharge, the discharge power is 14 W, which is lower than the 35 W of N<sub>2</sub> plasma without solid CO<sub>2</sub> particle, owing to the large amount of solid CO<sub>2</sub> and the high impedance of solid CO<sub>2</sub>. As the elapsed time increases, the solid CO<sub>2</sub> sublimates owing to Joule heating, causing a void to form around the discharge wire. The voids cause a decrease in the impedance, which increases the discharge power, resulting in an increase in the CO concentration. After 15 min, the discharge power reaches 35 W, which is the same as that of the N<sub>2</sub> plasma. As shown in Fig. 5 (a)–(c), as the N<sub>2</sub> flow rate is increased, there is no significant change in the CO<sub>2</sub> sublimation rate; therefore, there is no significant change in the discharging power.

Fig. 6 (a) and (b) show the waveforms of the voltage  $V$ , current  $I$ , and instantaneous power at a solid CO<sub>2</sub> filling range of  $x = 0$ –100 mm, pulse frequency of 210 Hz, N<sub>2</sub> flow rate of 1.0 L min<sup>-1</sup>, and elapsed times of (a) 1 min and (b) 7 min. The discharge mode is pulsed DBD. The discharge power averaged over time, as shown in Fig. 4, is determined by integrating the instantaneous power of the positive region as an effective power throughout a single cycle and then multiplying it by the pulse frequency  $f$  and conversion factors of the current and voltage probes. As shown in Fig. 6 (a), discharge occurs even in the early stages because it occurs in areas where dry ice particles are not present in the discharge region. As the elapsed time and discharge

power increase, the width of the current increases. This indicates that as the discharge region increases, the energy supplied to the molecules by the discharge increases, and the CO concentration increases.

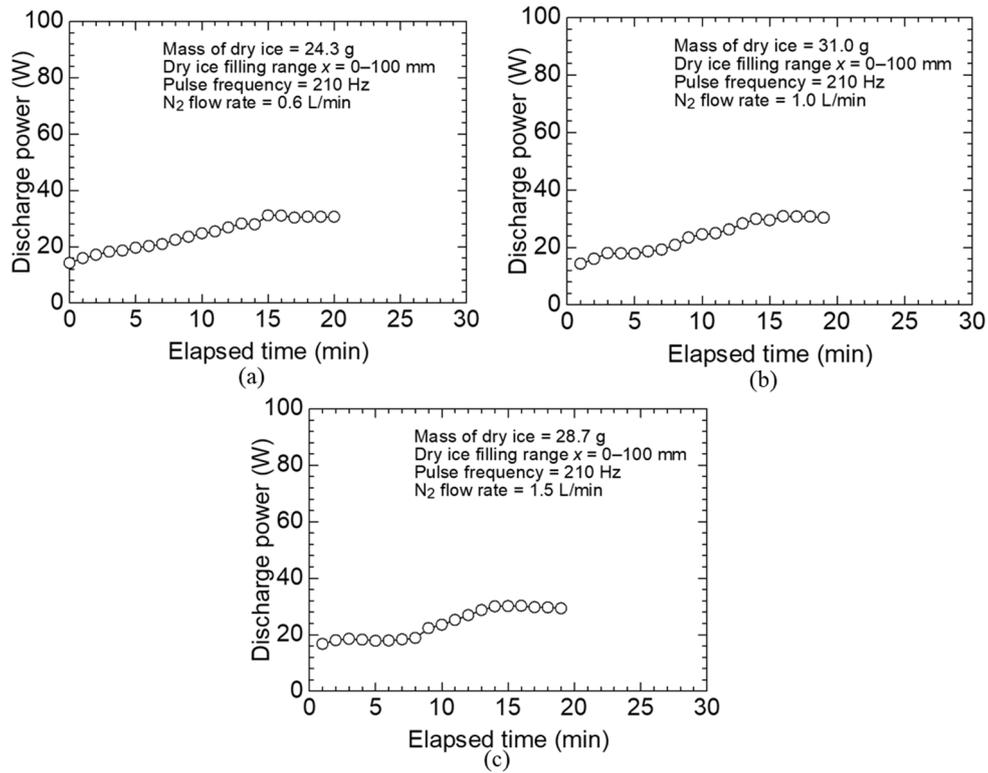


Fig. 5. Time-dependent discharge power at  $f = 210$  Hz,  $x = 0-100$  mm, and (a)  $N_2 = 1.0$  L  $min^{-1}$ , (b)  $N_2 = 1.0$  L  $min^{-1}$ , (c)  $N_2 = 1.0$  L  $min^{-1}$ .

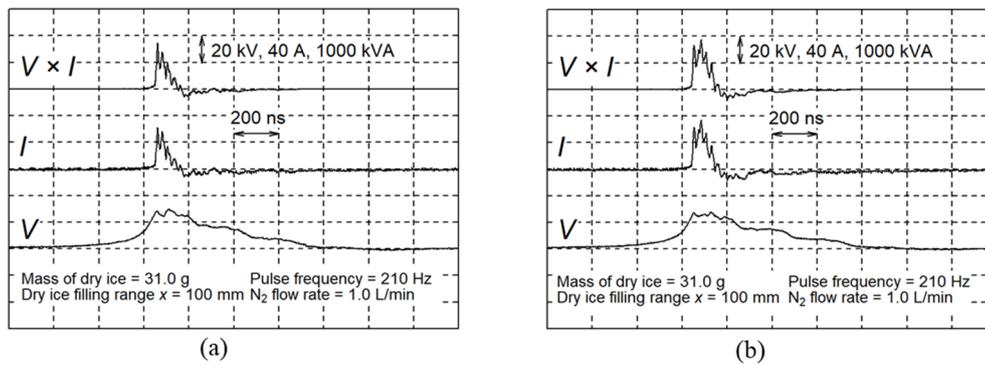
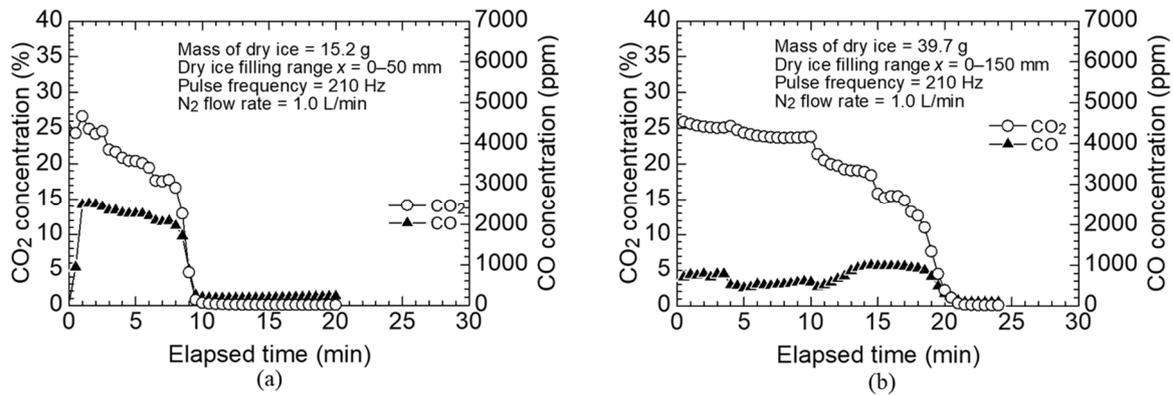


Fig. 6. Waveforms of the voltage  $V$ , current  $I$ , and instantaneous power at a solid  $CO_2$  filling range of  $x = 0-100$  mm, a pulse frequency of 210 Hz,  $N_2$  flow rate of 1.0 L  $min^{-1}$ , and elapsed time of (a) 1 min and (b) 7 min.

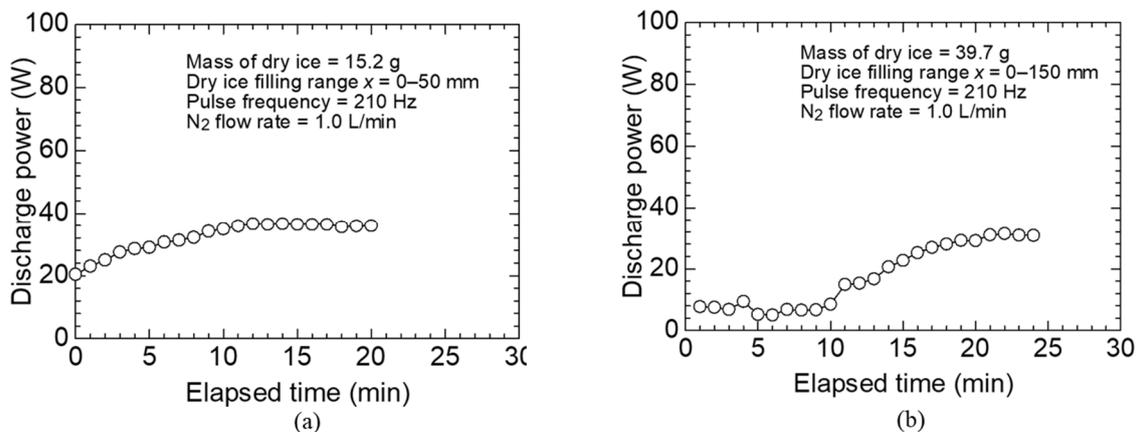
### 3.2 Effect of $CO_2$ particle filling volume on CO and $CO_2$ concentration

Figs. 7 (a) and (b) show the experimental results of the time-dependent  $CO_2$  and CO concentrations for a pulse frequency of 210 Hz, an  $N_2$  flow rate of 1.0 L  $min^{-1}$ , and solid  $CO_2$  filling ranges of (a)  $x = 0-50$  mm and (b)  $x = 0-150$  mm. As shown in Fig. 7 (a), the initial concentration of  $CO_2$  is 25%, which decreases until a treatment time of 10 min, after which no  $CO_2$  is detected. CO is generated immediately after the start of the discharge, reaching a maximum of 2500 ppm and decreasing as  $CO_2$  decreases. The maximum  $CO_2$  flow rate is 0.37 L  $min^{-1}$  at 1 min. As shown in Fig. 7 (b), the initial concentration of  $CO_2$  is 26%, which decreases until the treatment time of 21 min, after which no  $CO_2$  is detected. CO is generated immediately after the start of the discharge, gradually increases, reaches a maximum of 1000 ppm at 15 min, and then decreases. The maximum  $CO_2$  flow rate is 0.36 L  $min^{-1}$  at 1 min and the average  $CO_2$  flow rate is 0.34 L  $min^{-1}$  for 0-10 min.



**Fig. 7.** Time-dependent  $\text{CO}_2$  and  $\text{CO}$  concentrations at  $f = 210$  Hz,  $\text{N}_2 = 1.0$  L  $\text{min}^{-1}$ , and (a)  $x = 0\text{--}50$  mm and (b)  $x = 0\text{--}150$  mm.

Figs. 8 (a) and (b) show the discharge power for a pulse frequency of 210 Hz, an  $\text{N}_2$  flow rate of 1.0 L  $\text{min}^{-1}$ , and solid  $\text{CO}_2$  filling ranges of (a)  $x = 0\text{--}50$  mm and (b)  $x = 0\text{--}150$  mm. As shown in Fig. 8 (a), the initial discharge power is 20 W, increasing to 12 min and remaining steady at 37 W. Visual observation of the discharge region above the reactor confirms that the plasma produced strong light around the discharge wire and near the inner wall of the quartz tube, whereas weak light is observed between the  $\text{CO}_2$  particles. As shown in Fig. 8 (b), the initial discharge power is 8 W. The discharge power does not increase until 10 min, and then increases and becomes steady at 31 W for 21 min. This is because the amount of  $\text{CO}_2$  filling is high, and it takes time for the  $\text{CO}_2$  particles to sublime near the inner wall of the quartz tube. As shown in Fig. 7 (b),  $\text{CO}_2$  decreases from 10 to 15 min, but the increase in  $\text{CO}$  concentration is caused by an increase in the discharge power owing to the creation of a sufficient gas-phase gap on the inner wall of the quartz tube to promote discharge. However, the decrease in  $\text{CO}$  concentration compared to that shown in Fig. 7 (a) is caused by the greater impact of the decrease in  $\text{CO}_2$  concentration than the increase in  $\text{CO}$  concentration that can be expected from the increase in discharge power.

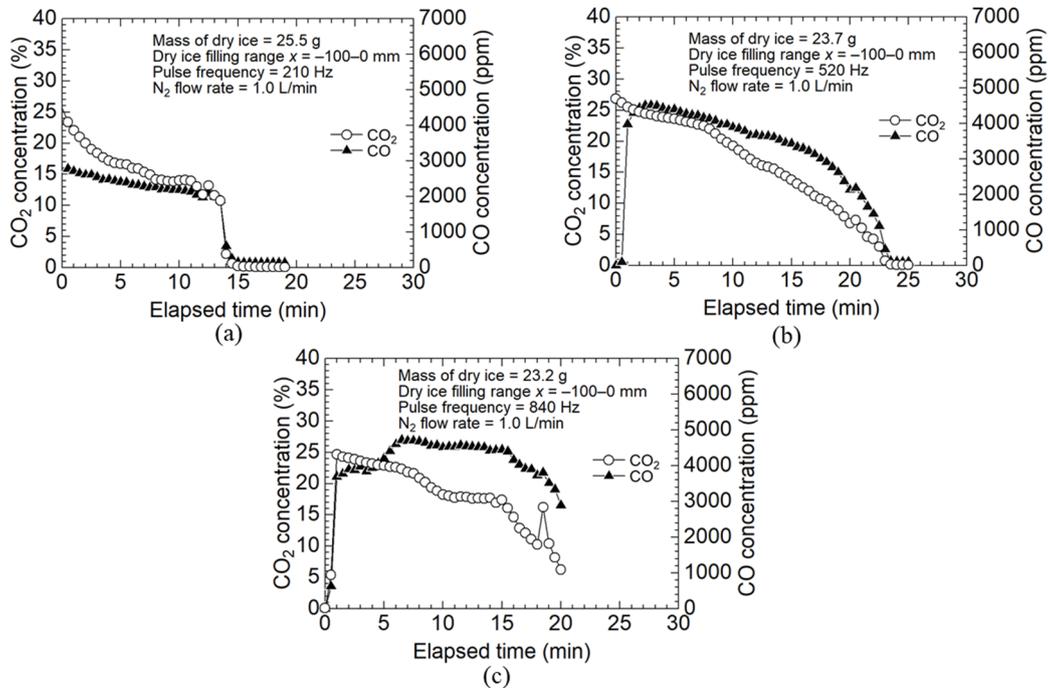


**Fig. 8.** Time-dependent discharge power at  $f = 210$  Hz,  $\text{N}_2 = 1.0$  L  $\text{min}^{-1}$ , and (a)  $x = 0\text{--}50$  mm and (b)  $x = 0\text{--}150$  mm.

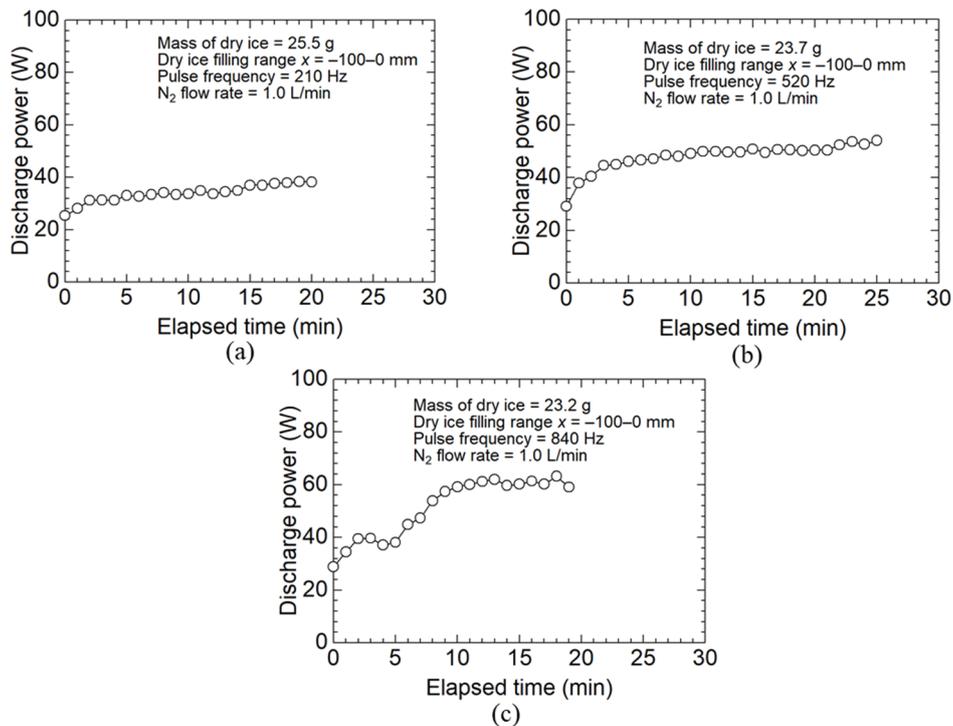
### 3.3 Effect of $\text{CO}_2$ particle filling upstream of the reactor on $\text{CO}$ and $\text{CO}_2$ concentration

The results shown in Figs. 4 and 7 reveal that expanding the discharge area and increasing the  $\text{CO}_2$  concentration leads to an increase in the  $\text{CO}$  concentration. To establish a synergistic relationship with the cooling effect of solid  $\text{CO}_2$  particles, experiments in which solid  $\text{CO}_2$  particles are filled upstream of the discharge area are conducted. Figs. 9 (a)–(c) show the experimental results of time-dependent  $\text{CO}_2$  and  $\text{CO}$  concentrations for a solid  $\text{CO}_2$  filling range of  $x = -100\text{--}0$  mm upstream of the reactor, an  $\text{N}_2$  flow rate of 1.0 L  $\text{min}^{-1}$ , and (a) pulse frequency of 210 Hz, (b) 520 Hz, and (c) 840 Hz. As shown in Fig. 9 (a), the initial concentration of  $\text{CO}_2$  is 24%, which decreases until a treatment time of 15 min, after which no  $\text{CO}_2$  is detected.  $\text{CO}$  is generated immediately after the start of the discharge, reaching a maximum of 2780 ppm and decreasing

as CO<sub>2</sub> decreases. The residence time at the maximum CO concentration is 0.06 s. From Fig. 9 (b), the initial concentration of CO<sub>2</sub> is 27% and decreases until the treatment time of 23 min, after which no CO<sub>2</sub> is detected. CO is generated immediately after the start of the discharge, reaching a maximum of 4506 ppm and decreases as CO<sub>2</sub> decreases. As shown in Fig. 9 (c), the initial concentration of CO<sub>2</sub> is 27% and decreases after 20 min. In this case, the measurement was stopped after 20 min because the reactor temperature reached the thermal resistance of the insulator. CO is generated immediately after the start of the discharge, reaching a maximum of 4716 ppm and decreasing as CO<sub>2</sub> decreases.



**Fig. 9.** Time-dependent CO<sub>2</sub> and CO concentrations at  $x = -100-0$  mm,  $N_2 = 1.0$  L min<sup>-1</sup>, and (a)  $f = 210$  Hz, (b)  $f = 520$  Hz, and (c)  $f = 840$  Hz.



**Fig. 10.** Time-dependent discharge power at  $x = -100-0$  mm,  $N_2 = 1.0$  L min<sup>-1</sup>, and (a)  $f = 210$  Hz, (b)  $f = 520$  Hz, and (c)  $f = 840$  Hz.

Figs. 10 (a)–(c) show the discharge power during the experiment for a solid CO<sub>2</sub> filling range of  $x = -100-0$  mm upstream of the reactor, an N<sub>2</sub> flow rate of 1.0 L min<sup>-1</sup>, and (a) pulse frequency of 210 Hz, (b) 520 Hz, and (c) 840 Hz. In Fig. 10 (a), the initial discharge power is 25 W, which increases up to 15 min and is steady at 38 W. The discharge power increases over time even without solid CO<sub>2</sub> particles in the discharge region, because the solid CO<sub>2</sub> particles lower the temperature of the gas in the discharge region and ground electrode, resulting in a decrease in electrical conductivity and increase in impedance. As the elapsed time increases, the temperatures of the quartz tube and ground electrode increase owing to the heat from the discharge, and the impedance decreases, resulting in an increase in the discharge power. In Fig. 10 (b), the initial discharge power is 29 W, which then increases gradually and saturates at 51 W after 11 min. In Fig. 10 (c), the initial discharge power is 28 W, which then increases gradually and saturates at 61 W at 11 min. As the pulse frequency increases to 210, 520, and 840 Hz and the discharge voltage decreases to 26, 23, and 22 kV, the discharge power increases, but not proportionally. When solid CO<sub>2</sub> is filled upstream of the reactor, the CO concentration increases due to the higher discharge power from the beginning and the increased residence time of gaseous CO<sub>2</sub>. The discharge power and CO concentration increase with increasing pulse frequency.

### 3.4 CO conversion and energy efficiencies

Fig. 11 shows the conversion efficiency  $\alpha$  and energy efficiency  $\eta$  versus specific energy  $E_v$  for the experiment using solid CO<sub>2</sub> and the reduction of gaseous CO<sub>2</sub> using cylinder gas. Because CO<sub>2</sub> and CO concentrations are unsteady in elapsed time due to CO<sub>2</sub> sublimation,  $\alpha$  and  $\eta$  here denote the  $\eta$  that reaches a maximum during the treatment time and  $\alpha$  at that time. As  $E_v$  increases,  $\alpha$  increases because more energy is given to the CO<sub>2</sub> molecules.  $\eta$  is a function of  $\alpha$  and  $E_v$  as shown in Eq. (5), and in this study range,  $\eta$  decreases as  $E_v$  increases because  $E_v$  varies more than  $\alpha$ . The results of the experiment using cylinder gas at a CO<sub>2</sub> concentration of 20%, which is equivalent to the CO<sub>2</sub> produced during solid CO<sub>2</sub> reduction, show a high  $E_v$  owing to the absence of solid CO<sub>2</sub>, which decreases the impedance in the reactor and increases the discharge power. Comparing the case with the same  $E_v$ , solid CO<sub>2</sub> filled upstream of the discharge area of the reactor ( $x = -100-0$  mm), N<sub>2</sub> flow rate 1.0 L min<sup>-1</sup>, and discharge frequency 520 Hz with cylinder gas and discharge frequency 210 Hz, the energy efficiency  $\eta$  is 2.7% and 2.3%, respectively, and the conversion efficiencies  $\alpha$  are 1.8% and 1.4%, respectively. The introduction of solid CO<sub>2</sub> upstream of the reactor increases  $\alpha$  and  $\eta$  by 0.4% each. This is because the solid CO<sub>2</sub> cools the reactor and promotes reduction. However, when the discharge area is filled with solid CO<sub>2</sub>, the results show a similar trend to those obtained with cylinder gas. This is because of the large impedance of solid CO<sub>2</sub>, which results in a lower discharge power, and it is difficult to achieve the effect of promoting reduction at low temperatures. These results show that filling solid CO<sub>2</sub> upstream of the discharge region ( $x = -100-0$  mm), decreasing the N<sub>2</sub> flow rate, increasing the discharge frequency, and increasing  $E_v$  increases  $\alpha$  and  $\eta$ .

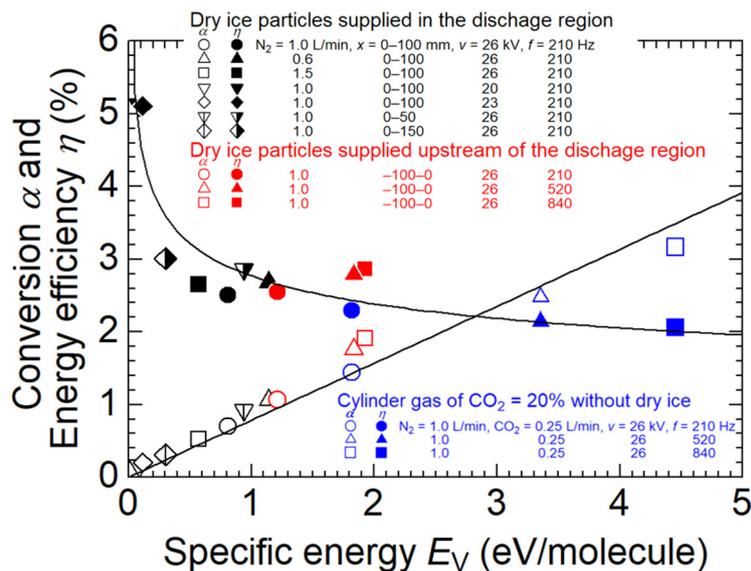


Fig. 11. Relationships between specific energy ( $E_v$ ), conversion efficiency ( $\alpha$ ), and energy efficiency ( $\eta$ ).

## 4. Conclusion

To improve the energy efficiency of CO<sub>2</sub> reduction, solid-phase CO<sub>2</sub> reduction using a DBD reactor was performed by varying the gas flow rate, applied voltage frequency, and dry ice introduction point. The main results are summarized as follows:

1. Joule heat, rather than forced thermal convection, is dominant the solid CO<sub>2</sub> sublimation, and CO is generated immediately after discharge. When the N<sub>2</sub> flow rate is 0.6 L min<sup>-1</sup> at a pulse frequency of 210 Hz and the solid CO<sub>2</sub> filling range of  $x = 0\text{--}100$  mm, CO<sub>2</sub> and CO reach 26% and 3147 ppm, respectively. As the N<sub>2</sub> flow rate decreases, the CO concentration increases because the residence time in the reactor increases.
2. When the N<sub>2</sub> flow rate is 1.0 L min<sup>-1</sup> at a pulse frequency of 210 Hz and the solid CO<sub>2</sub> filling range of  $x = 0\text{--}50$  mm, CO<sub>2</sub> and CO reach 25% and 2500 ppm, respectively, and the decrease in the solid CO<sub>2</sub> filling volume decreases the impedance and increased the discharge power. Therefore, even when the solid CO<sub>2</sub> filling volume is increased, the amount of CO is lower because of the decrease in discharge power.
3. When dry ice is filled upstream of the discharge region, the CO concentration increases due to higher discharge power and increased residence time of gaseous CO<sub>2</sub>, achieving a maximum energy efficiency  $\eta$  of 2.8% and conversion efficiency  $\alpha$  of 1.9%.
4. Comparing solid CO<sub>2</sub> filled upstream of the discharge region of the reactor ( $x = -100\text{--}0$  mm) with cylinder gas at the same  $E_v (= 1.8$  eV/molecule),  $\eta$  was 2.7% and 2.3% and  $\alpha$  was 1.8% and 1.4%, an increase of 0.4%, respectively. Both  $\eta$  and  $\alpha$  increase due to the cooling of the reactor by the solid CO<sub>2</sub> particles.

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