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Carbon dioxide conversion by means of coplanar dielectric barrier discharges*

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Abstract. To face the worldwide problem of anthropogenic carbon dioxide (CO_2) emission new techniques have to be developed. One approach for carbon capture utilization (CCU) is the conversion of CO_2 to more valuable chemicals, e.g., carbon monoxide (CO) by means of non-thermal plasma generated at ambient conditions and supplied by excess energy from renewable sources. This paper reports about the effect of the admixture of inert gases, namely nitrogen or argon to CO_2 in a coplanar dielectric barrier discharge (DBD). Systematic experiments were conducted to investigate the effects of applied voltage, frequency, flowrate and CO_2 concentration in the influent. The composition of products, energy efficiency and yield were determined. Within the investigated parameter ranges, the maximum conversion of CO_2 to CO efficiency of 1% was achieved when the specific input energy was 190 J L^{-1}, whereas the maximum CO yield of 0.7% was achieved when the specific input energy was 210 J L^{-1}. In conclusion, the energy efficiency can be significantly increased by operating the plasma in a diluted CO_2 gas.

1 Introduction

Global warming is one of the most important issues for the 21st century. According to the intergovernmental panel on climate change (IPCC) the most of the global warming is due to the emission of greenhouse gases by human activities [1]. Worldwide the emission of anthropogenic carbon dioxide (CO_2) is about 30 billion tons per year. One way to prevent a rise up of this emission is to improve the efficiency of final energy consumption. More efficient industrial processes, e.g., through better chemical catalysts, energy savings in buildings and transport sector, can make the greatest contribution to reduce emissions (about 50% of the 450-Scenario) [2]. In addition to an increase in energy efficiency two further possibilities for reductions in CO_2 emissions have been considered; the storage of CO_2 (CCS: carbon capture and storage) as well as the use of CO_2 (CCU: carbon capture and utilization). In the CCU approach CO_2 is sequestrated and then converted into different chemicals that can be stored or used commercially.

In the 1990's different approaches on CO_2 reforming by means of plasmas, also combined with catalyst have been studied [3]. However, low energy yields were obtained. Nevertheless, the progressive use of renewable energies (wind, water, solar, etc.) contributes its part to the reduction of the emission of greenhouse gases, but can also be seen as a cheap source of energy for plasma operation. This gives the possibility for an energy-to-gas solution. Lebouvier et al. [4] discuss how CO_2 dissociation could provide a new route for Syngas production. They suggested the use of plasma sources as an alternative solution to the already established and industrially used methods, such as: auto-thermal natural gas reforming and coal gasification. Additionally, they compared different plasma sources and reported all their benefits and limitations. A common drawback is that the highest energy efficiency is accomplished at the lowest conversion rate, and the latter is also inversely proportional to the total flow-rate of the gas.

Although there are several examples reported in the literature about the utilization of plasma sources for the dissociation of CO_2 such as dielectric barrier discharges (DBDs) [5–7], microwave plasma [8] and corona discharge [9]. the systematic variation of the dilution gas and its effect on the overall process is only rudimentary studied.

The objective of this work was to determine if the energy efficiency of CO_2 dissociation in a coplanar DBD can be improved by changing the composition of the gas, in particular the admixture of the inert gases nitrogen or argon. A coplanar arrangement was chosen for two main reason: the metal electrodes are not exposed to the

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discharge area and because of proven easy scalability [10]. Additionally, the products of the dissociation are investigated in detail because they or their intermediates could be used as precursors for the production of other value added chemicals, e.g., methanol.

2 Experimental setup

The plasma source is sketched in Figure 1. It is a dielectric plate with embedded coplanar electrode geometry [10]. The discharge arrangement consists of a rectangular ceramic base body made of a mixture of silicon and aluminum oxide ($125 \times 35 \times 2.4$ mm). In order to realize the coplanar electrode arrangement two copper electrodes are interleaved (intersperse) at intervals $g = 0.5$ mm next to each other on the base body. The dielectric covering the electrodes is the same as the body material. As seen in Figure 1, at the two ends of the ceramic base plate, the electrodes are not covered by dielectric, which allows the contacting of the electrodes to the electric power supply. This specific arrangement offers two advantages among other discharge arrangements. Both electrodes are covered with a dielectric, i.e., erosion and oxidation processes at the metal electrodes cannot take place. On the other hand, this discharge form allows a very compact design that can be relatively easily scaled to larger volume flow rates (e.g., by cascading or stacking individual modules).

The discharge cell was mounted in a gas-tight housing made of Teflon. Its upper part has been provided with a notch to accommodate the discharge cell. In the lower part a recess has been made to allow the electrical connections. At the narrow ends of the housing two holes are machined for gas inlet and outlet. The housing was closed in the bottom part with a Teflon plate and in the top part with a plexiglas plate to enable visual observation of the discharge. In order to keep the system closed Teflon sealing was placed in between the upper plate and the housing body and then all bolted together on the lower part. Because the gas flow could pass along the plates, no significant back-pressure was obtained.

The reactor, as seen in Figure 2, was operated with a sinusoidal voltage generated with a programmable AC source (Chroma model 61604) and a high voltage transformer. To measure the voltage a high voltage probe (Tektronix P6015A) was used, to measure the charge a 150 pF capacitor was connected in series to ground. Both the signals of voltage and charge were recorded with an oscilloscope (Tektronix DPO4104) and allowed the determination of injected discharge energy per AC cycle by charge-voltage-plots (E_{cyc}, so-called Lissajous-figure method). The power input delivered into the coplanar discharge reactor P was calculated integrating the area of the charge-voltage-plot and multiplying the resulting value by the frequency (f) of the applied voltage signal: $P = E_{\mathrm{cyc}} f$.

The reactor was connected to a gas flow line made of perfluoro-alchoxy (PFA) tubing (6 mm OD, 4 mm ID). The mole fraction of CO_2 (99.995% purity, Air Liquid) in N_2 (99.999% purity, Air Liquide) or Ar (99.999% purity, Air Liquide) were adjusted as the total flowrate using mass flow controllers (MFCs, Bronkhorst). The effluent gas was then analyzed with an FT-IR (Thermo Scientific, Antaris IGS Analyzer) equipped with a long-path gas cell of 2 m length. The gas cell was heated at 80 °C to avoid any condensation and also to not destroy ozone. Downstream the FT-IR there was an oxygen sensor (Zirox, SGM7) and an ozone monitor (Anseros, MP-6020) for quantitative analysis.

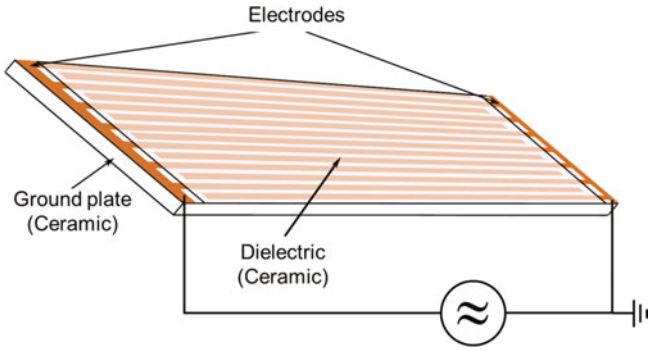

Fig. 1. Schematic representation of the coplanar discharge arrangement (the upper dielectric layer is here only for explanatory purpose transparent).

The experimental parameters that were varied systematically are: frequency of the sinusoidal applied voltage, total flowrate and CO_2 concentration. In order to obtain comparable results of the measurements all the experiments were performed at the same high voltage amplitude of 17 $kV_{p\text{-}p}$. With 100% CO_2 the applied voltage to ignite and sustain a discharge in the reactor is higher than with pure N_2 or Ar, but 17 $kV_{p\text{-}p}$ ensure that the plasma is developed over the entire electrode surface for all gas compositions.

3 Results

3.1 CO production

For any given experimental condition the efficiency of the process was analyzed by monitoring the amount of CO formed as a function of the specific input energy (SIE), which is the energy deposited in the reactor per gas volume, and was calculated as follows:

$$\mathrm{SIE(J\ L^{-1})} = \frac{P(W)}{\mathrm{Flow\ rate(L\ s^{-1})}}. \quad (1)$$

Figure 3 reports the production of CO as a function of SIE. The CO concentration increased with SIE for all gas mixtures being investigated. At the same SIE, changing the CO_2 concentration in N_2 from 10% to 30% resulted in an increasing CO production (Fig. 3a). The concentration of CO was similar for CO_2 concentrations between 30% and 50%. In pure CO_2 the lowest amount of CO was obtained. Thus, the total concentration of CO_2 in N_2 strongly affects the CO production. No distinct effect of the flow rate was observed.

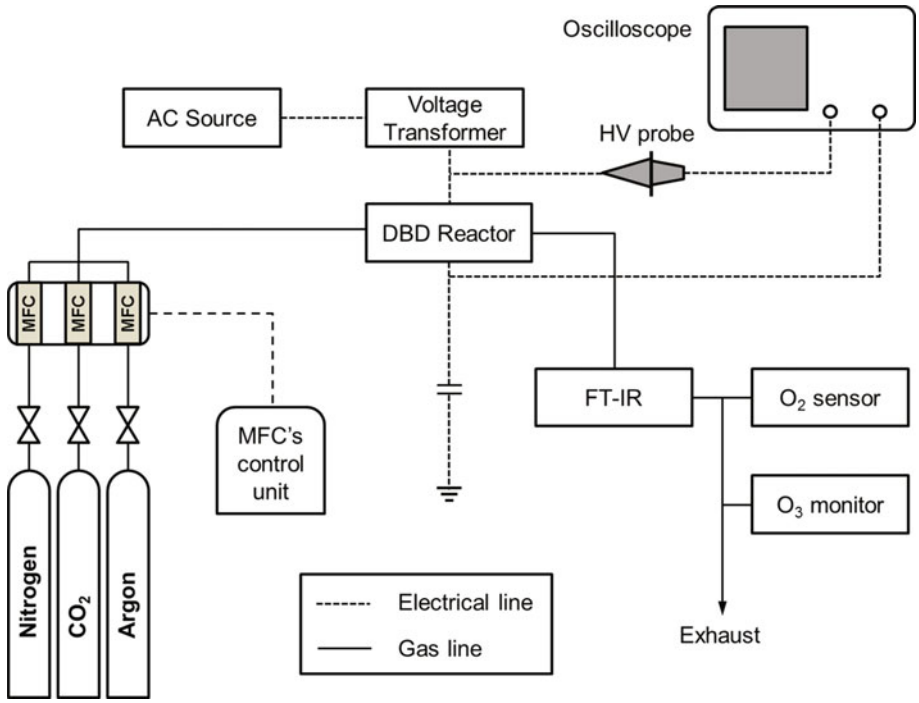

Fig. 2. Schematic representation of the experimental setup.

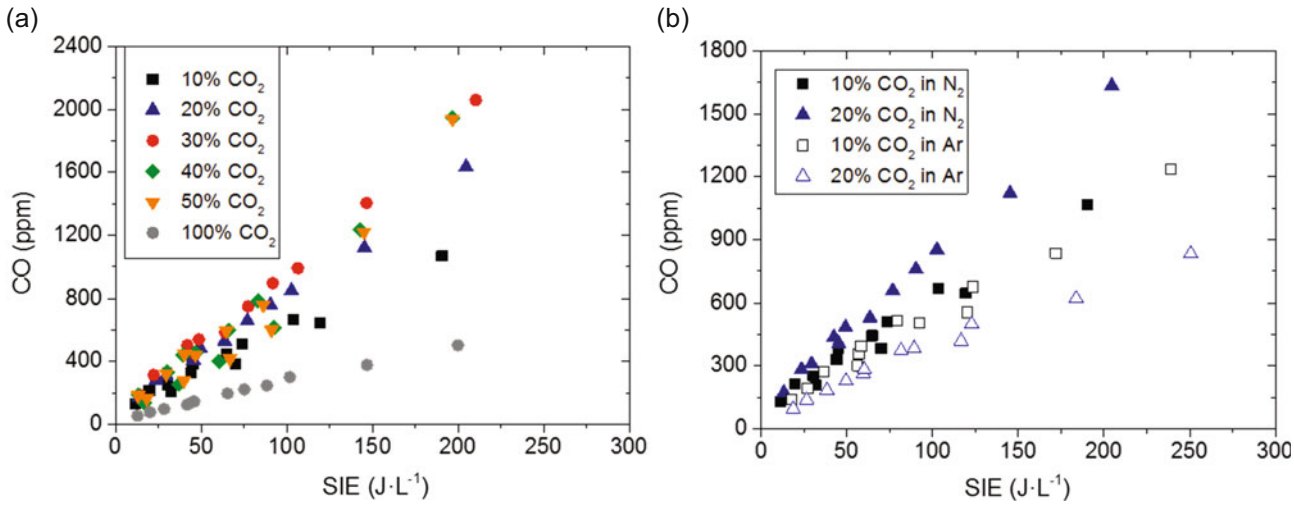

Fig. 3. CO production at different concentration of CO_2 in N_2 and Ar.

Figure 3b reports a comparison between N_2 and Ar as dilution gas. With 10% CO_2 there is no difference between N_2 and Ar. But with 20% CO_2 it is possible to produce more CO in the mixture with N_2 than with Ar. In both the graphs the error bars are not reported in order to make it easier to read the data. For the values of SIE the obtained error is of 5% while for CO concentration is 3%. No distinct effect of the flow rate was observed.

3.2 Analysis of the O-containing species

Beside CO, oxygen and ozone were identified as products of the plasma chemistry. Despite other studies, the concentration of each specie was measured and monitored. No NO, NO_2, or N_2O was detected. The detection limits for the above mentioned species are 4, 2 and 1 ppm respectively. The other possible nitrogen oxides that could be formed in a plasma are: N_2O_4 and N_2O_5. Both are not detected with the analytical system used in this research.

Figure 4a reports the concentration of O_2 as a function of SIE. Oxygen was measured by the oxygen sensor which operates similar as a lambda probe. However, the data in Figure 4a were corrected with respect to a calibration with a CO_2-O_2-CO gas which considers the conversion of O_2 with CO to CO_2 at the zirconia surface in the measuring device. As observed for CO (Fig. 3a), changing the CO_2 concentration in N_2 from 10% to 30% resulted in an increased O_2 production. The concentration of O_2

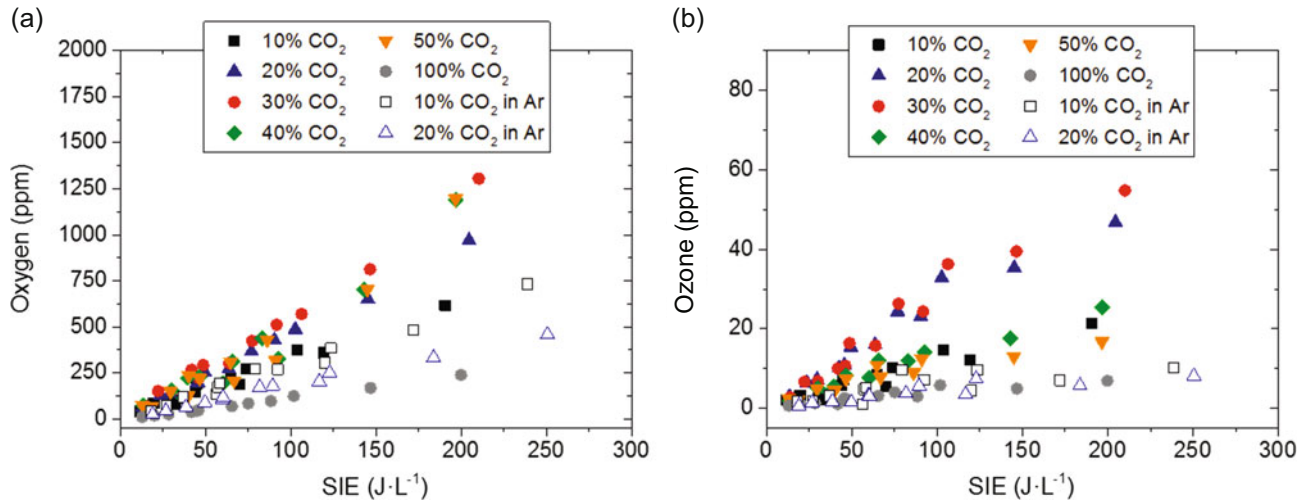

Fig. 4. Oxygen (a) and ozone (b) production in the different experimental conditions tested.

is similar for CO_2 concentrations between 30% and 50%. In pure CO_2 the lowest amount of O_2 is obtained. The same trend is obtained when Ar is used as dilution gas. At 10% CO_2 there is no significant difference and at 20% CO_2 in N_2 the more O_2 is produced. The results obtained for O_2 production are thus comparable to the ones for CO production which is obvious due to dissociation of CO_2.

A complete different scenario was observed in the case of ozone (O_3) formation. The production of O_3 as a function of SIE is reported in Figure 4b. At 10%, 40% and 50% of CO_2 in N_2 the concentration of O_3 is nearly equal. At 20% and 30% of CO_2 in N_2 the highest production of O_3 was observed. In pure CO_2 the lowest amount of O_3 was observed. When Ar is used the concentration of O_3 is nearly equal to the one obtained in pure CO_2.

Figure 5a reports the ratio CO/O_2 as a function of SIE. The ratio decreases with SIE for every CO_2 concentration. The stoichiometric value is 2 (marked by the red line). For each given CO_2 concentration at the lowest SIE the value of the ratio is bigger than 2. When N_2 is used as dilution gas, the stoichiometric value is reached at SIE of 50 J L^{-1}, but after this value the ratio becomes lower. When Ar is used as dilution gas, the stoichiometric value is reached at SIE of 60 J L^{-1} for 10% CO_2 and 120 J L^{-1} for 20%. In pure CO_2 the value is reached only at the highest SIE which is 200 J L^{-1}. The error for O_2 concentration is of 3% while for O_3 is of 2%.

Considering that also O_3 was produced with this plasma source (see concentrations in Fig. 4b), an atomic oxygen amount was calculated as follows:

$$Ox = 2O_2 + 3O_3 \quad (2)$$

In the equation (2) only oxygen and ozone are considered. When N_2 is used as dilution gas several different nitrogen oxides also contribute to the oxygen balance. However, any NO, NO_2, or N_2O was detected. Figure 5b reports the ratio CO/Ox as a function of SIE. The ratio decreases with SIE for every CO_2 concentration. The stoichiometric value is 1 (marked by the red line). For each given CO_2 concentration at the lowest SIE the ratio is higher than the stoichiometric value, i.e., that not all oxygen atoms generated by CO_2 dissociation are converted into O_2 and O_3. As no other oxygen containing by-products are obtained the fate and processes remain unclear. When N_2 is used as dilution gas, the stoichiometric value is reached for a relative low value of SIE (25–50 J L^{-1}), but after this value the ratio becomes lower. When Ar is used as dilution gas, the stoichiometric value is reached at 60 J L^{-1} for 10% CO_2 and 120 J L^{-1} for 20%. In pure CO_2 the value is reached only at the highest SIE which is 200 J L^{-1}.

3.3 Performance of the plasma source

In order to better compare the energy efficiency obtained in different experimental conditions the energy yield (EY) of CO production as defined in the following equation was calculated:

$$\mathrm{EY(g\ kW\ h^{-1})} = \frac{3.6 \times C_{CO}(\mathrm{ppm})\, M_w(\mathrm{g\ mol^{-1}})}{V_m(\mathrm{L\ mol^{-1}})\, \mathrm{SIE(J\ L^{-1})}}. \quad (3)$$

C_{CO} is the concentration of CO produced at a certain value of SIE. M_w is the molar mass of CO and V_m is the molar volume of the gas mixture at atmospheric condition.

Figure 6 reports the value of EY as function of SIE obtained at different concentration of CO_2. The EY decreases with SIE. At the same value of SIE, changing the CO_2 concentration in N_2 from 10% to 30% resulted in higher EY (Fig. 6a). The EY is decreasing for CO_2 concentrations between 30% and 50%. Also in this case the total concentration of CO_2 in N_2 strongly affects EY. Additionally, an effect on the flowrate has to be mentioned. For 20% and 30% of CO_2 there is no significant effect due to the flowrate. At 10% the highest value of EY for 200 and 300 L h^{-1} than for 100 L h^{-1} was observed. Thus, there is a clear effect of gas retention time in the reactor. The values of CO_2 concentration of 40% and 50% are characterized by the occurrence of a different pattern: at 100 and 300 L h^{-1} is not possible to see a strong effect

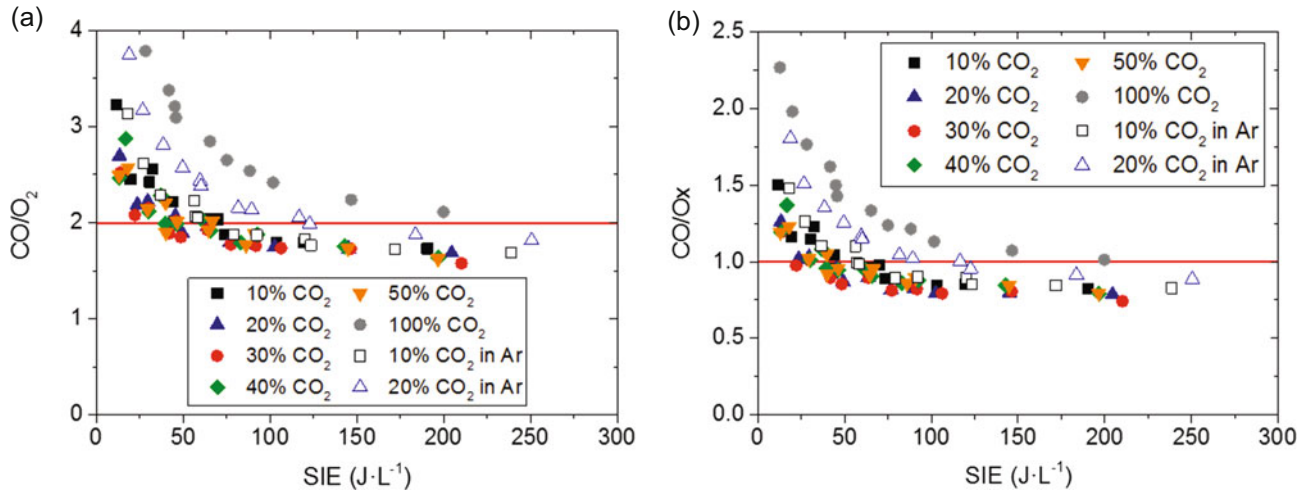

Fig. 5. (a) CO/O_2 ratio and (b) CO/Ox ratio depending on SIE and gas composition. The red lines mark the corresponding stoichiometric values.

while at 200 L h^{-1} the value of EY is lower at the same value of SIE.

Figure 6b reports the value of EY as a function of SIE when Ar is used as dilution gas and a comparison with N_2 admixture. The EY is less than with N_2 in both the case of 10% and 20% CO_2 concentration. In pure CO_2 the lowest EY is obtained. Despite with N_2, in Ar the dependence on the SIE is less marked but still present and the more energy is supplied to the system the less is the EY. Also in this case there is no flow effect for 20% but the same behavior for 10% where the lowest amount of EY is reached for the lowest flowrate. Ar as dilution gas is not significantly improving the EY compared to pure CO_2 as it is for N_2.

4 Discussion

The energy efficiency of CO_2 dissociation by means of coplanar DBD can be improved by using a gas admixture of nitrogen or argon. N_2 produce a better effect in terms of energy efficiency and conversion rate than Ar. Within the different experimental parameters investigated the maximum conversion rate in N_2 is 1% which was achieved with quite moderate SIE, namely 190 J L^{-1} and at the CO_2 concentration of 10%. The maximum CO yield of 0.7% was achieved with 210 J L^{-1} SIE and at the CO_2 concentration of 30%. The maximum conversion rate in Ar is 1.2 % which was achieved with 250 J L^{-1} and at CO_2 concentration of 10%.

The energy efficiency evaluated through EY results in values up to 60 g kW h^{-1}, where the highest value is achieved with 30% CO_2. At a fixed value of CO_2 concentration the highest energy efficiency is achieved at the lowest SIE and conversion rate, while the highest conversion rate is achieved at highest SIE and lowest energy efficiency as reported also by other works [4–6].

Increasing the CO_2 concentration resulted in a decreased CO formation when Ar is used as dilution gas. These results were also obtained by Zheng et al. [5]. In their work they reported that the conversion rate decreased from 9.5% to 3.9% when the CO_2 concentration was from varied from 1% to 4% in Ar at constant voltage and power. They reported also the EY in the same range of concentration changed from 13.2 to 20.7 g kW h^{-1}. In the case of this research the higher conversion rate is observed at 10% CO_2 in Ar. A possible explanation given by Zheng et al. [5] on the observed effect is that Ar is an atomic gas which can undergo excitation or complete ionization by electrons with sufficient energy, while CO_2 is a polyatomic molecule that will be also vibrational excited at much lower electron energies, and consequently could be dissociated [11]. The most probable scenario is at first when the plasma is generated there is production of high-energy electrons. These electrons are able to ionize Ar atoms instead of CO_2 molecules. The subsequent energy transfer from excited (metastable) Ar to CO_2 to get the latter ionized and dissociated is decreased when the concentration of CO_2 is increased. An additional comparison could be done considering the results of Wang et al. [6]. In this study a glow discharge plasma was investigated and as dilution gas they utilized He, also an atomic gas. When the concentration of CO_2 was varied from 1% to 10% they also observed an increase of the burning voltage and the conversion rate decreased from 21.2% to 6.9%. It is not possible to make any comparison in terms of conversion rate between the two plasma sources investigated by Zheng et al. [5] and Wang et al. [6] because of different reactor sizes, reactor materials and different values of SIE.

In the work of Brehmer et al. [8] the case of 100% CO_2 is studied and an EY of 4.1 g kW h^{-1} is obtained with a conversion rate of 4.5% and SIE of 45 kJ L^{-1}. On the other hand it is possible to achieve at the best condition a value of 11.2 g kW h^{-1} with a conversion rate of 0.2% and SIE of 780 J L^{-1}.

Taylan and Berberoglu [9] investigated the CO_2 dissociation with a micro-hollow cathode discharge arrangement and DC high-voltage power supply. In case of

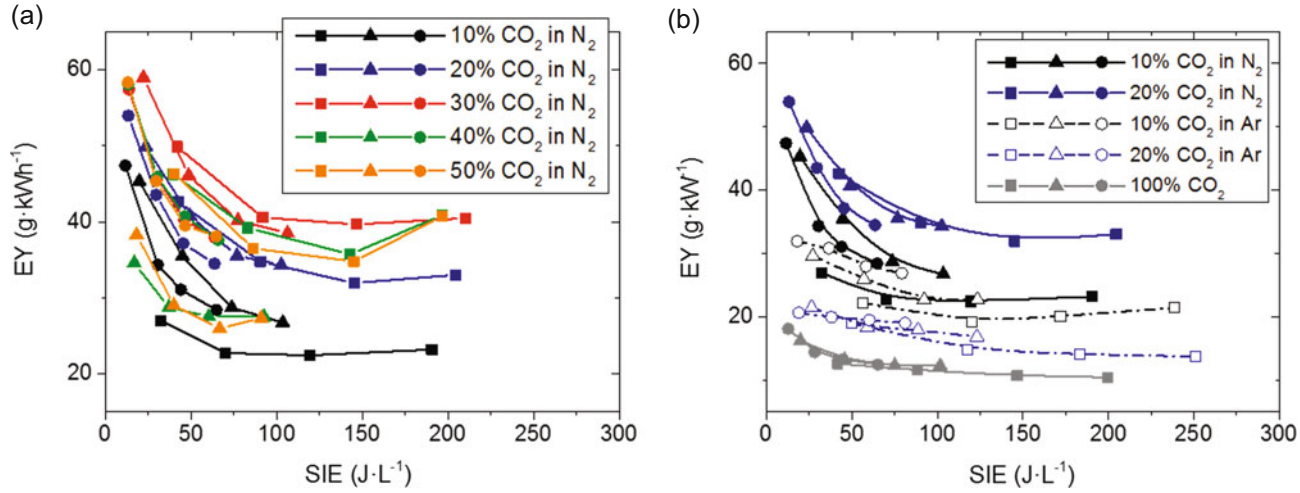

Fig. 6. Energy yield at different concentration of CO_2 in N_2 (a) as well as N_2 and Ar (b). Squares are related to 100 L h^{-1}, triangles to 200 L h^{-1} and circles to 300 L h^{-1} flowrate.

100% CO_2 they obtained a value of EY of 49.4 g kW h^{-1} with a conversion rate of 1.8% and SIE of 1.54 kJ L^{-1}, while on the other hand when the conversion rate is 10.5% at SIE of 14.9 kJ L^{-1} the EY is 29.1 g kW h^{-1}.

Recently, Ramakers et al. [7] reported results on the CO_2 dissociation with a DBD plasma source. They investigated the conversion rate and energy efficiency when CO_2 is diluted in He or Ar. They reported that at 100% CO_2 the conversion rate was 5.1% while at 5% CO_2 in He was 5.7% and at 5% CO_2 in Ar was 5.3%. When all these results are converted in terms of EY in pure CO_2 a value of 28.4 g kW h^{-1} is obtained. In 5% Ar the value of EY is 29.2 g kW h^{-1} and in 5% He is 30.2 g kW h^{-1}. Additionally, a detailed explanation was given after presenting charge-voltage-plots and current profiles. They considered that at lower CO_2 concentration the breakdown voltage is lower and this resulted in a wider and extended area filled with plasma. The latter enhances the CO_2 conversion. In the case of this research the applied voltage was kept constant in every condition to ensure a full coverage of the dielectric. The findings of Ramakers et al. [7] are confirmed since at lower voltage in pure CO_2 the plasma area is smaller than when it is diluted with N_2 or Ar. And also, the more CO_2 is diluted the broader is the area filled with plasma.

Additionally Ar has an ionization potential of 15.76 eV while He has 24.58 eV. Considering the ionization potential the comparison could be made better between Ar and N_2 with a value of 15.58 eV. However, as demonstrated by this research the effect on the conversion rate observed when CO_2 is diluted in N_2 or Ar are different. With both gases as dilution media the conversion rate is decreasing when CO_2 concentration and flowrate are increasing. The main difference between the two gases is that with N_2 is possible to obtain higher energy efficiency at the concentration of CO_2 of 30%. It is not possible at this stage of the research to provide a detailed insight on the effect of N_2 as dilution gas. Future investigations have to be performed including the utilization of different plasma sources in order to confirm the results presented in this work. Additionally, of further interest would be the combination of the experimental results with simulations.

5 Conclusion

This paper experimentally demonstrated the dissociation of CO_2 using a coplanar dielectric barrier discharge reactor at atmospheric pressure. Moreover, this study reported a better effect in terms of energy efficiency (EY) and conversion rate in the presence of N_2 instead of pure CO_2. The use of a different dilution gas such as Ar is not giving the same enhancement of CO_2 dissociation to CO as with N_2.

The results in terms of EY are promising with values up to 60 g kW h^{-1} even if the conversion efficiency is about 1%. Additionally, the stoichiometric ratio CO/O_2 is achieved with relatively low SIE (50 J L^{-1}) at 30% CO_2 in N_2. At this SIE and CO_2 concentration the EY is relatively high (about 48 g kW h^{-1}). Considering the small and compact size of the plasma reactor a possible solution to increase the conversion rate could be to connect several elements in series and/or parallel.

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