

Influence of liquid water and hydrogen on CO₂ conversion for a nanosecond-pulsed DBD

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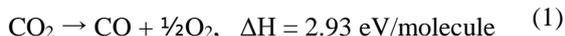
Abstract: CO₂ was converted in a nanosecond-pulsed DBD, operated at atmospheric pressure and ambient temperature. Mixtures of CO₂ with Ar and H₂ were investigated. In addition, the influence of liquid water on the conversion was studied. Introducing water into the reactor contributed to a decrease in CO₂ conversion. However, the main product was always CO with the highest amount of 4.4% for the dry operation. Increasing the concentration of Ar in the feed gas resulted in a drop in CO₂ conversion and CO production.

Keywords: CO₂ conversion, nanosecond-pulsed DBD, H₂O, plasma in liquid, CO₂ reduction

1. Introduction

The concentration of the major man-made greenhouse gas CO₂ in the atmosphere is significantly growing due to the ongoing combustion of fossil fuels and rapid industrialization around the world. Therefore, innovative and novel technologies are needed to reduce the emitted CO₂ and ideally utilize emissions. As a carbon source, the gas could be used for the production of fuels and other value-added chemicals, e.g. methanol (CH₃OH) [1-8].

However, CO₂ is a highly stable molecule and for the activation and breaking of double bonds (C=O=O), a high amount of energy is needed as demonstrated by Equation 1 [1,2]:



Non-thermal plasma (NTP) has been reported as a promising approach for the conversion of CO₂ at atmospheric pressure and room temperature. Gaseous species can be dissociated and activated to generate energetic electrons and other reactive species. Accordingly, dielectric barrier discharge (DBD) [1-6], microwave discharge [1,2], gliding arc discharge [1,2], and nanosecond-pulsed (NSP) discharge have been studied for CO₂ conversion [1,2]. The different approaches are still being optimized with respect to operating parameters and configurations.

For the here presented approach, a DBD was operated with nanosecond high-voltage pulses. Different mixture ratios of H₂/CO₂ with and without the addition of deionized water and Ar were investigated. Especially the contribution of water was of interest to determine if it would be suitable as an alternative and cheap hydrogen source for the production of oxygenates or syngas. Further interesting were liquid products, e.g. formate, as energy stores and base substances. To the best of our knowledge, this is the first study with this objective.

2. Materials and Methods

The coaxial DBD configuration was powered by the positive nanosecond high-voltage pulses with a pulse duration of 500 ns and amplitude of 20 kV, respectively. Pulses were applied with a repetition rate of 1 kHz. The

mixtures of CO₂, H₂, and Ar were fed to the DBD with the fixed flow rate of 30 ml/min. At first, the ratio of H₂:CO₂ was varied from 0:1 to 7:1 while the Ar concentration was fixed at 20%. This experiment was carried out for dry (only gas) operation and in the presence of deionized water. Subsequently, Ar concentrations of 40% and 50% were investigated for specific H₂:CO₂ ratios. The gaseous products were analysed by FTIR while liquid products were determined by Ion Chromatography.

Dissipated power, P , depending on pulse repetition rate, f , was derived from measurements of current, I , and voltage, V , according to Equation 2:

$$P = f \cdot \int V \cdot I \, dt \quad (2)$$

From the FTIR results, absolute and effective CO₂ conversion, $X_{\text{CO}_2, \text{abs}}$, and $X_{\text{CO}_2, \text{eff}}$, were calculated with Equations 3 and 4 [1,2]. $[\text{CO}_2 \text{ in}]$ and $[\text{CO}_2 \text{ out}]$ designate the concentrations of CO₂ before and after plasma treatment.

$$X_{\text{CO}_2, \text{abs}} (\%) = \frac{[\text{CO}_2 \text{ in}] - [\text{CO}_2 \text{ out}]}{[\text{CO}_2 \text{ in}]} \cdot 100\% \quad (3)$$

$$X_{\text{CO}_2, \text{eff}} = \frac{X_{\text{CO}_2, \text{abs}} \cdot [\text{CO}_2] (\%)}{100} \quad (4)$$

O₂ concentration was calculated from Equation 5:

$$[\text{O}_2] = \frac{[\text{CO}] - [\text{H}_2\text{O}]}{2} \quad (5)$$

The Specific Energy Input, SEI, depending on the gas flow rate, F , and the energy efficiency of the conversion, η , were described by Equations 6 and 7.

$$\text{SEI} (kJ \cdot l^{-1}) = \frac{P (kW)}{F (l \cdot \text{min}^{-1})} \cdot 60 (s \cdot \text{min}^{-1}) \quad (6)$$

$$\eta (\%) = X_{\text{CO}_2, \text{eff}} \cdot \frac{\Delta_R H^0 (kJ \cdot \text{mol}^{-1})}{\text{SEI} (kJ \cdot l^{-1}) \cdot 24.5 (l \cdot \text{mol}^{-1})} \quad (7)$$

A reaction enthalpy, $\Delta_R H^0$, of $279.8 \text{ kJ}\cdot\text{mol}^{-1}$ (2.9 eV) is assumed for the splitting of a CO_2 molecule. The value of $24.5 \text{ l}\cdot\text{mol}^{-1}$ is strictly valid only for atmospheric pressure and a temperature of 298 K.

3. Results and Discussion

Deionized water was introduced to the reactor by a peristaltic pump with a flow rate of 1.4 ml/min. For a H_2 concentration increasing from 0 to 70% ($\text{H}_2:\text{CO}_2$ ratios of 0:1 to 7:1), effective CO_2 conversion and energy efficiency are shown in Fig. 1. The Ar admixture was kept constant at 20%. Effective CO_2 conversion highly depended on the $\text{H}_2:\text{CO}_2$ ratio. However, a clear trend could not be determined. For dry and wet, i.e. with water, operation, the highest amount of conversion was achieved when there was no hydrogen in the gas mixture. The results for an increasing H_2 concentration were likewise inconclusive. In the absence of H_2 , the highest conversion was 5.5% for the dry operation and 3.2% in the presence of water (at an $\text{H}_2:\text{CO}_2$ ratio of 1:1). The general characteristic was similar for both conditions. The decrease in the CO_2 conversion with water could be a result of an unstable discharge behavior [7]. Moreover, the reaction between CO and water contributes to the back reaction and a decreasing conversion.

The results further show the influence of higher Ar admixtures for some particular ratio of $\text{H}_2:\text{CO}_2$. Increasing

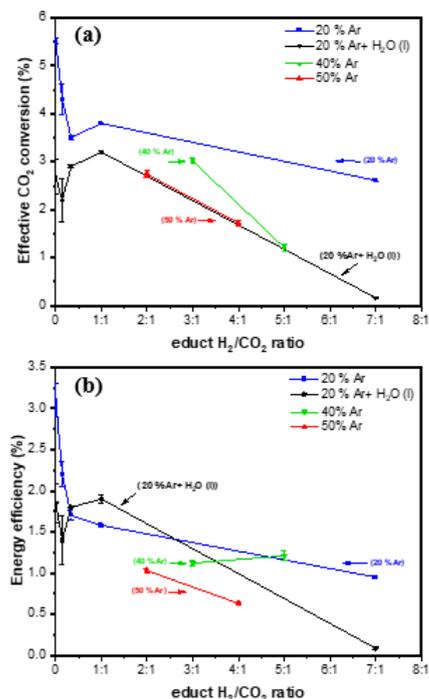


Fig. 1. Effective CO_2 conversion (a), $X_{\text{CO}_2, \text{eff}}$, and energy efficiency (b), η , for dry operation and in the presence of water, and for different concentrations of Ar as a function of the $\text{H}_2:\text{CO}_2$ ratio.

the concentration of Ar was again resulting in decreasing conversion. The actual highest conversion was achieved for 20% Ar and no admixture of H_2 . The findings are contradicting the results previously reported by Zeng et al. [8]. They observed that rising concentrations of Ar were helpful to achieve a higher conversion.

The results for energy efficiency (Fig. 1b) demonstrate that by increasing the concentration of CO_2 , the energy efficiency decreased sharply, particularly for the dry operation. However, in the presence of water, the energy efficiency is similar to values obtained for a dry conversion at an $\text{H}_2:\text{CO}_2$ ratio of 1:1 (H_2/CO_2), i.e. corresponding to the highest achieved conversion (c.f. Fig. 1a).

Fig. 2 shows the production of CO, and H_2O , as obtained from FTIR measurements, and the calculated production of O_2 . The production of CO (Fig. 2a) followed the same

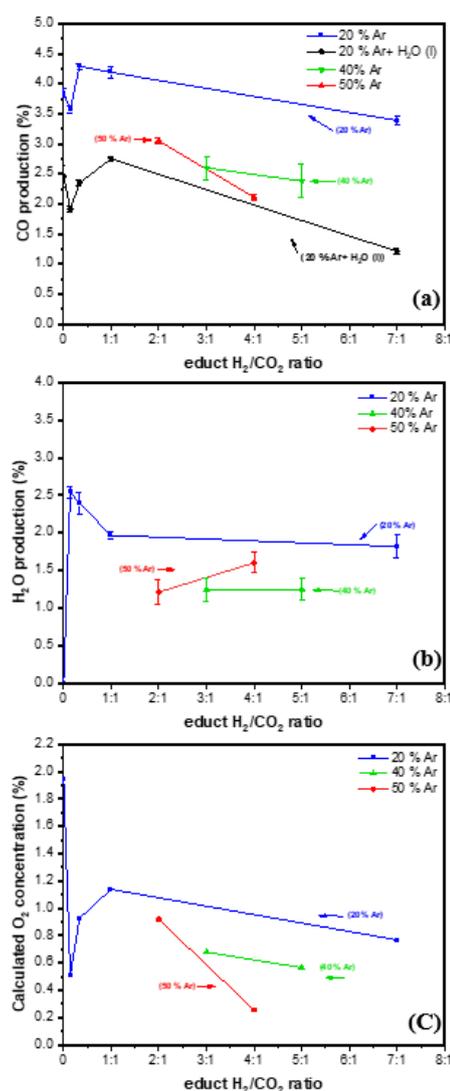


Fig. 2. Concentration of measured production of CO (a), H_2O (b) and calculated production of O_2 (c) for dry operation and in presence of water for different concentrations of Ar as a function of $\text{H}_2:\text{CO}_2$ ratios.

trend as the CO₂ conversion for similar H₂:CO₂ educt ratios. The dry operation was again superior. The highest CO production of 4.4% was observed at 20% of H₂ and 60% of CO₂ (a ratio of 0.33:1) with 20% of Ar. With water, the maximum amount of 2.7% was achieved for a CO₂:H₂ ratio of 1:1. Fig. 2b shows the water concentration after the reaction in the gas phase, indicating that at 20% of Ar, more water was produced with the highest amount of 2.5% in the presence of 20% of H₂ and 60% of CO₂ (i.e. a ratio of 0.33:1). Stoichiometrically, the amounts of produced CO and H₂O were supposed to be similar but deviating values were measured. This suggests the production of O₂, which is set free and can be calculated from Equation 5 and as shown in Fig. 2c.

The production of O₂ suggests two reactions for CO₂, i.e. CO₂ dissociation (Equation 1) and CO₂ reduction (CO₂ + H₂ ⇌ CO + H₂O), occurring in parallel, as a result of the reaction of CO₂ and H₂. It should be mentioned that a little amount of CH₄ in the range of ppm was also observed.

Interestingly, in the liquid samples, analysed by Ion Chromatography, only formate was found in a concentration of 0.25 mg/L (data not shown) for an H₂:CO₂ ratio of 1:1. For other ratios no liquid products were detected.

The concentration ratios after passing through the reactor are far from thermodynamic conditions. However, the thermodynamically calculated concentrations for CO₂, CO, and O₂ show qualitatively similar behaviour as shown in Fig. 3. Accordingly, the behaviour can be approximately described by Equation 8, where p is a partial pressure of the compound and K is the thermodynamic equilibrium constant:

$$K = \frac{p[\text{CO}] \cdot p[\text{H}_2\text{O}]}{p[\text{CO}_2] \cdot p[\text{H}_2]} \quad (8)$$

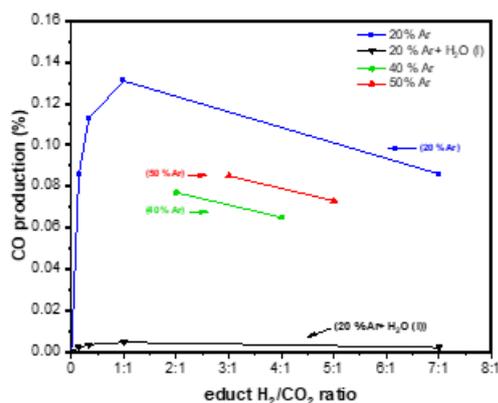


Fig. 3. Thermodynamic calculation of CO concentration as a function of H₂:CO₂ ratio.

As Fig. 3. indicates, the highest concentration of CO of 0.13% was observed at 20% of Ar for an H₂:CO₂ ratio of 1:1. Although the calculated values were lower than the ones obtained for the plasma treatment (Fig. 2a), both thermodynamically calculated and plasma treatment

results followed approximately the same trend. The reason for having a greater amount by the plasma treatment can be explained by in-coupling electrical work and heat.

4. Summary and Outlook

The effects of an addition of H₂, liquid water, and Ar addition were studied for the conversion of CO₂ with a DBD, which was operated by nanosecond high-voltage pulses. The introduction of H₂ and water influence the conversion process. Firstly, CO₂ conversion in the presence of water resulted in lower conversion. Secondly, irrespective of dry operation or within the presence of water, the behaviour of the reactor changed for different ratios of H₂ and CO₂. The highest conversion was achieved for a ratio of 1:1. Increasing the amount of Ar in the gas mixture lead to a decrease in the conversion and chemical production in general, which contradicts other studies. The discrepancy can be explained and confirmed by calculations on the production of O₂. Although CO₂ conversion and CO production were lower in the presence of water, further investigations are required to improve the efficiency and the conversion process for these conditions. Moreover, changing electrical parameters, e.g. pulse amplitude and pulse length, as well as introducing buffer solutions, could increase the formation of formate as an interesting liquid product and improve CO₂ conversion.

5. Acknowledgment

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6. References

- [1] A. George, *Renewable Sustainable Energy Rev.*, **135**, 109702 (2021).
- [2] R. Snoeckx, *Chem. Soc. Rev.*, **46**, 5805 (2017).
- [3] Lan L, *Catal. Commun.*, **130**, 105761 (2019).
- [4] Aerts R, *ChemSusChem* **8**, 702 (2015).
- [5] A. Ozkan, *Plasma Sources Sci Technol.*, **25**, 055005 (2016).
- [6] D. Mei, *J. CO2 Util.*, **62**, 102073 (2022).
- [7] R. Snoeckx, *ChemSusChem* **10**, 409 (2016).
- [8] Y. Zeng, *J. Phys. D: Appl. Phys.*, **50**, 184004 (2017).