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CO_2–CH_4 conversion and syngas formation at atmospheric pressure using a multi-electrode dielectric barrier discharge

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ABSTRACT

The conversion of CO_2 and CH_4 into value-added chemicals is studied in a new geometry of a dielectric barrier discharge (DBD) with multi-electrodes, dedicated to the treatment of high gas flow rates. Gas chromatography is used to define the CO_2 and CH_4 conversion as well as the yields of the products of decomposition (CO, O_2 and H_2) and of recombination (C_2H_4, C_2H_6 and CH_2O). The influence of three parameters is investigated on the conversion: the CO_2 and CH_4 flow rates, the plasma power and the nature of the carrier gas (argon or helium). The energy efficiency of the CO_2 conversion is estimated and compared with those of similar atmospheric plasma sources. Our DBD reactor shows a good compromise between a good energy efficiency and the treatment of a large CO_2 flow rate.

1. Introduction

Almost 72% of the total greenhouse effect is attributed to water vapor and clouds, the remainder being mainly the result of CO_2 [1]. Natural greenhouse gas emissions are responsible for bringing the average temperature of the Earth to +15 °C (instead of −18 °C) by absorbing its infrared radiation. However, anthropogenic activities reinforce this situation, leading to an increase of greenhouse gas concentrations in the atmosphere [2,3]. In that respect, carbon dioxide (but also methane) figures among the most important greenhouse gases produced by industries and taking part to the global warming. Its production has increased for many decades. Today, it represents 29 gigatons of emission per year and is expected to increase to 36 or 43 gigatons/year, depending upon the energy world policies, i.e. how we will use existing and new energy sources [4]. For this reason, the remediation of CO_2 has received increasing attention in recent years.

Until now, four approaches have been considered to reduce the industrial CO_2 footprint: using renewable energy, using non-carbon energy resources, CO_2 capture and CO_2 reforming [5–7]. The latter approach aims at using carbon dioxide as a feedstock and transforming it into value-added products such as carbon monoxide and oxygen, as shown in (1).

$$CO_2 \rightarrow \frac{1}{2}O_2 + CO \quad \Delta G^0_{298\,K} = +257.2 \text{ kJ mol}^{-1} \tag{1}$$

This aforementioned reaction is thermodynamically limited and highly endothermic. According to Le Chatelier's principle, a high reaction temperature and a low CO_2 partial pressure are required to achieve a high conversion [7–9]. Owing to the high thermodynamic stability of the CO_2 molecule in standard conditions, its dissociation can only be achieved through endothermic reactions requiring an external energy source. In that respect, conventional chemistry processes have already been used, such as electroreduction of CO_2 [6]. Besides, non-thermal atmospheric plasma processes can be employed such as corona discharges [10,11], dielectric barrier discharges (DBD) [12–18], gliding-arcs [19,20] and plasma jets [21,22]. Low pressure plasma sources can also be used such as microwave discharges [23,24]. Among these sources, most of the energy required for the dissociation of CO_2 depends on the electron energy distribution function (EEDF). Carbon dioxide can be mixed with methane to form carbon monoxide and molecular hydrogen in (2), but also other products of interest can be formed, such as oxygenated organic molecules and hydrocarbons [25,26].

$$CO_2 + CH_4 \rightarrow 2H_2 + 2CO \quad \Delta G^0_{298\,K} = 170.8 \text{ kJ mol}^{-1} \tag{2}$$

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The conversion of CO_2 and CH_4 by an atmospheric dielectric barrier discharge (DBD) is reported in this study, using Ar as a carrier gas to generate more metastable species and therefore stabilize the discharge. Using a tubular DBD offers a promising and innovative solution since the transformation of CO_2 can be performed "on line", i.e. directly at the output of industrial chimneys instead of releasing the CO_2 into the atmosphere and hence increase the greenhouse effect. Therefore, it does not require capture, transport or storage of CO_2 and, for instance, could partially close the carbon loop if coupled to green electricity. By using gas chromatography (GC), we demonstrate that this process is efficient to obtain CO and value-added products. Three parameters are evaluated: the CO_2 and CH_4 flow rates, the power supplied to the DBD and the nature of the carrier gas (Ar or He). The energy efficiency of the CO_2 conversion is estimated and compared with those of similar plasma sources.

2. Experimental set-up

2.1. DBD reactor

A cylindrical multi-electrode DBD reactor dedicated to the treatment of elevated gas flow rates has been designed as shown in Fig. 1. It consists of a 2 mm thick tube made in quartz with an external diameter of 34 mm and a length of 100 mm (so as to ensure a long residence time). The gas enters via 16 inlets of 0.75 mm in diameter arranged into a circular pattern, then travels longitudinally through the tubular reactor and finally flows out of the reactor via 16 outlets (same configuration as the inlet). The discharge is generated between six AC high-voltage tubular electrodes set at equal distance from a central tubular electrode which is grounded. The power applied to the high-voltage electrodes is provided by an AFS Generator G10S-V with a maximum power of 1000 W and a variable frequency in the range between 1 and 30 kHz. The distance between the grounded electrode and each high-voltage electrode is the same as the distance between two high-voltage electrodes, namely 3 mm. The grounded electrode is a copper rod with a diameter of 5 mm and a length of 100 mm, while the high-voltage electrodes are copper wires approximately 1 mm in diameter and with the same length of 100 mm. The high-voltage electrodes are encompassed into alumina dielectric tubes with 0.75 mm thickness, as depicted in Fig. 1.

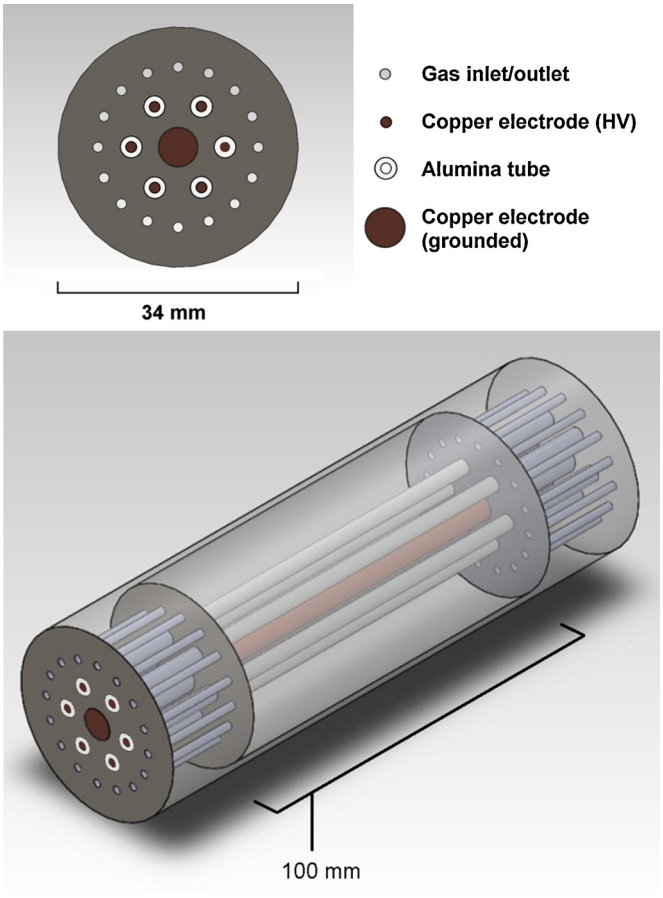

Fig. 1. Schematic diagram of the DBD reactor.

2.2. Entire set-up

A schematic of the entire experimental setup is shown in Fig. 2. Argon, carbon dioxide and methane are introduced into the reactor via Aalborg volumetric flow meters able to measure flow rates as high as 1800, 120 and 120 mL min^{-1}, respectively. Argon (or helium) is used as the carrier gas to initiate and maintain the discharge. The total flow rate of the gas mixture supplying the DBD reactor remains fixed at 1920 mL min^{-1} while the CO_2 and CH_4 flow rates are both varied from 0 to 120 mL min^{-1}.

The products resulting from the plasma phase reactions are analyzed downstream of the reactor with an online gas chromatograph (Agilent 6890N) equipped with a 60/80 Carboxen 1000 column (Supelco 1-2390-U). The products are analyzed with two detectors: a thermal conductivity detector (TCD) and a flame ionization detector (FID). The conversion of CO_2 and CH_4 are calculated according to Eqs. (3) and (4), respectively, where A represents the peak area assigned to CO_2 or CH_4 in the chromatogram:

$$CO_{2\text{Conversion}}\,(\%) = \chi_{CO_2} = \frac{A_{CO_2\text{ without plasma}} - A_{CO_2\text{ with plasma}}}{A_{CO_2\text{ without plasma}}} \times 100 \quad (3)$$

$$CH_{4\text{Conversion}}\,(\%) = \chi_{CH_4} = \frac{A_{CH_4\text{ without plasma}} - A_{CH_4\text{ with plasma}}}{A_{CH_4\text{ without plasma}}} \times 100 \quad (4)$$

The selectivities of H_2, O_2, CO, C_2H_6 and C_2H_4 have been calculated as reported in Table 1, listed as H, O or C based selectivities, depending on the plasma composition (CH_4, CO_2, CO_2/CH_4 respectively).

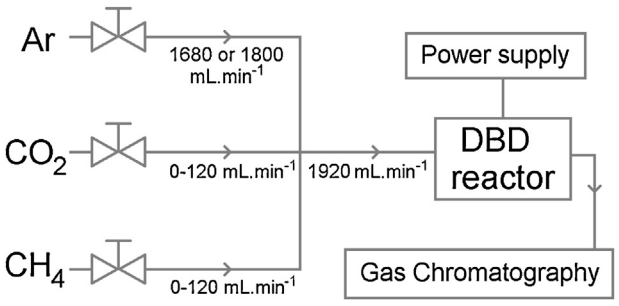

Fig. 2. Schematic diagram of the entire experimental set up.