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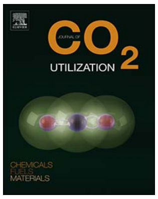

Carbon dioxide dissociation in a microwave plasma reactor operating in a wide pressure range and different gas inlet configurations

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ABSTRACT

Microwave (MW) plasmas represent a promising solution for efficient CO_2 dissociation. MW discharges are also very versatile and can be sustained at various pressure and gas flow regimes. To identify the most favorable conditions for the further scale-up of the CO_2 decomposition reaction, a MW plasma reactor operating in pure CO_2 in a wide pressure range (200 mbar–1 bar) is studied. Three different gas flow configurations are explored: a direct, reverse and a vortex regime. The CO_2 conversion and energy efficiency drop almost linearly with increasing pressure, regardless of the gas flow regime. The results obtained in the direct flow configuration underline the importance of post-discharge cooling, as the exhaust of the MW plasma reactor in this regime expanded into the vacuum chamber without additional quenching. As a result, this system yields exhaust temperatures of up to 1000 K, which explains the lowest conversion (~3.5% at 200 mbar and 2% at 1 bar). A post-discharge cooling step is introduced for the reverse gas inlet regime and allows the highest conversion to be achieved (~38% at 200 mbar and 6.2% at 1 bar, with energy efficiencies of 23% and 3.7%). Finally, a tangential gas inlet is utilized in the vortex configuration to generate a swirl flow pattern. This results in the generation of a stable discharge in a broader range of CO_2 flows (15–30 SLM) and the highest energy efficiencies obtained in this study (~25% at 300 mbar and ~13% at 1 bar, at conversions of 21% and 12%). The experimental results are complemented with computational fluid dynamics simulations and with the analysis of the latest literature to identify the further research directions.

1. Introduction

The global need for efficient CO_2 utilization technologies recently highlighted new ideas for re-use and conversion of CO_2 waste streams into added-value products [1–5]. Multiple papers demonstrated the potential of different plasma systems for activation and dissociation of this highly inert gas [6–16]. In general, microwave (MW) discharges are considered to be one of the most promising plasma systems for CO_2 decomposition due to their capability to utilize the highly efficient vibrational excitation kinetics of the non-equilibrium discharge [10,17–19]. In this way, it is possible to realize CO_2 dissociation with a higher energy efficiency than in the conventional thermal process [5,20]. From a technological point of view, MW plasma systems represent an electrodeless solution with a high electric energy utilization efficiency and a fast switching on time [21]. Another advantage of CO_2 decomposition in a MW discharge reactor relates to the possibility to utilize electricity produced from renewable sources, thus balancing the power grid [3].

Historically the most successful experiments on CO_2 conversion in a MW discharge were performed in the 1980s in the USSR [20,22]. Energy efficiencies up to 90% were achieved when a supersonic flow regime was utilized at reduced pressure of about 200 mbar. The topic was brought up again more recently in response to the spread of intermittent renewable electricity sources and the general acceptance of the need to fight global warming. Attempts to reproduce the conditions and results reported in the work of Fridman *et al.* have been made, but energy efficiencies only up to 51% were demonstrated so far in this case [23]. Besides that, a lot of novel approaches to improve the performance of CO_2 decomposition in MW plasma systems were recently presented. Chen *et al.* reported a twofold increase of the conversion and energy efficiency when a NiO catalyst on a TiO_2 support was installed downstream of a surface-wave MW CO_2 discharge [24–26], reaching a conversion and energy efficiency of both 42%. Uhm *et al.* reported a high CO_2 conversion (45%, but with an energy efficiency of only 8%) for an atmospheric pressure MW plasma torch with a post-discharge coal powder gasification system [27]. Mitsingas *et al.* presented a highly

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efficient CO_2 dissociation process in a compact atmospheric pressure MW plasma reactor [28], achieving 50–80% energy efficiency, but at low conversion (9–3%). The introduction of gas admixtures to a CO_2 MW discharge could be used to achieve some degree of control over the plasma parameters and to utilize more efficient pathways for CO_2 decomposition. The influence of Ar [29,30], N_2 [31], H_2 [32,33] and H_2O [24–26,34] gas admixtures on CO_2 dissociation in a MW plasma was demonstrated experimentally and by modeling. Such research is also important for the future up-scaling of the process, as gas impurities are inevitable on an industrial scale.

Another ongoing research direction related to efficient CO_2 decomposition in a MW plasma is targeting *in-situ* diagnostics to allow a better understanding of the discharge mechanisms and process control [23,29,30,35,36]. Likewise, modeling has also proven to give valuable insight in the underlying mechanisms of CO_2 dissociation in a MW plasma, including the role of vibrational kinetics, and identifying the limitations in the conversion and energy efficiency in a wide range of conditions [17–19,31].

Despite all the recent attention to this technology, studies of the MW plasma operating in CO_2 in a broad range of process parameters and gas flow configurations are still rare. Usually only a very limited parameter range is presented. Moreover, given the development stage of the technology, it is still unclear which discharge conditions are the most beneficial for scale-up. In this paper, we utilize the opportunity to generate a stable MW discharge in pure CO_2 over a wide pressure range and with different gas inlet regimes to study the CO_2 conversion reaction in this broad range of conditions. Thus, the aim of this paper is to demonstrate the influence of pressure, gas flow configuration and post-discharge cooling on the CO_2 decomposition process in a MW discharge reactor. This work will be useful for further up-scaling of MW plasma systems, which will be necessary to bring plasma-based CO_2 conversion into real application.

2. Experimental

The experiments are performed in a MW plasma system composed of the commercial IPLAS *CYRANNUS* plasma source mounted on top of a stainless steel vacuum chamber (*cf.* Fig. 1). The principle of this MW plasma source is based on a resonator with annular slot antennas [37]. This special set-up allows to sustain a MW discharge in a very wide pressure range, from low (10^{-2} mbar) to atmospheric pressure (1 bar).

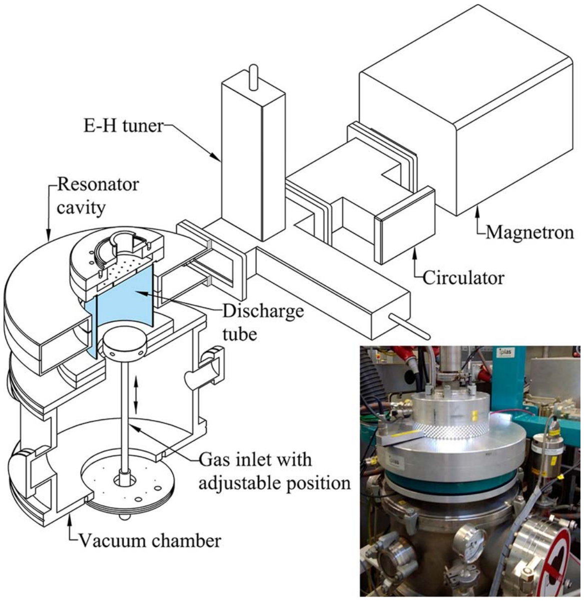

Fig. 1. Drawing and picture of the MW discharge system. The MW discharge tube is indicated with pale blue colour in the schematic drawing.

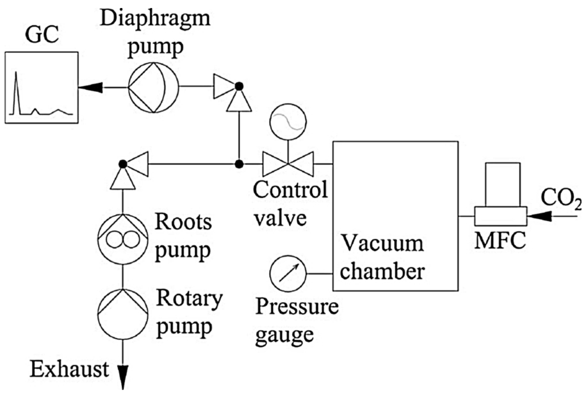

Fig. 2. Gas supply and vacuum scheme of the MW set-up used.

2.1. Microwave system

The 2.45 GHz magnetron supply with a maximum output of 6 kW microwave field is connected through a circulator and an E–H tuner to the resonator cavity. The plasma is formed in a cylindrical quartz tube with a diameter of 140 mm and a height of 140 mm, which corresponds to a volume of 2.1 l. The discharge tube is connected via a DN350 flange to a chamber with a height of 235 mm and overall volume of 22 liters. The reflected power is measured via the microwave detector installed in the circulator and minimized by the E–H tuner, which is used as an impedance matching device. The circulator, magnetron and the plasma-exposed parts of the discharge cell are all water-cooled, while the resonator and the outer surface of the quartz tube are air-cooled.

2.2. Gas supply and vacuum scheme

The gas supply and vacuum systems are shown in Fig. 2. Prior to operation, the vacuum chamber is pumped down to 20 mbar via a rotary and Roots pump installed in series. The pressure is set via a control valve and a pressure gauge, while CO_2 flow is supplied through a mass flow controller (MFC). With 2–6 kW MW power input the discharge can be ignited without an additional inert gas admixture or electric field concentrator at a maximum pressure of about 100 mbar when 5–30 SLM CO_2 is supplied to the system. After the breakdown, the pressure in the chamber can be further increased up to 1 bar, while the plasma remains to be sustained.

CO_2 dissociation is taking place in the plasma according to Reaction (1):

$$CO_2 \rightarrow CO + 0.5\,O_2, \quad \Delta\,H = 2.9\,\text{eV/molecule} \tag{1}$$

To evaluate the CO_2 conversion and corresponding energy efficiency in the MW discharge, the gas mixture is sampled from the exhaust pipe to the gas chromatograph (GC) through a diaphragm pump. The formulas below are used to calculate the CO_2 conversion (Eq. (2)), specific energy input (SEI, Eq. (3)) and energy efficiency of the process [38] (Eq. (4)):

$$CO_2\text{Conversion}(\%) = [1 - \frac{\text{moles}\,CO_{2,\,\mathit{Plasma\ ON}}}{\text{moles}\,CO_{2,\,\mathit{Plasma\ OFF}}}] \times 100\% \tag{2}$$

$$\text{SEI(eV/molec.)} = \frac{P_{Input}(W)\cdot 60(\text{sec/min})}{\mathit{Flow\ rate}(\text{ml/min})\cdot 3.92(\text{eV}\cdot\text{ml/J}\cdot\text{molec.})} \tag{3}$$

$$\text{Energy efficiency}(\%) = CO_2\text{Conversion}(\%)\cdot\frac{\Delta H\,(\text{eV/molec.})}{SEI\,(\text{eV/molec.})} \tag{4}$$

We use the input power in Eq. (3), and not the plasma power as is often done in the literature [23,26,32,35]. In some systems, like DBDs, the plasma power can be only half of the input power, but in the MW system, the difference is usually quite small (can be estimated to be around 10% [21]). Still, there are some losses due to the reflectance of