Investigation of an atmospheric 2.45 GHz microwave pressure CO_2 plasma source: comparison of pulsed and CW operation

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Abstract: A 2.45 GHz microwave CO_2 plasma is studied by means of optical emission spectroscopy, mass spectrometry and ICCD imaging near atmospheric pressure (i. e. 900 mbar). The aim is to determine the energy efficiency and conversion efficiency and the mechanisms behind the CO_2 dissociation. In the parameter range studied (flow between 10 and 100 slm, power between 900 W and 2700 W) the heavy particles in the plasma have been found to be internally in equilibrium, with $T_{vib} \approx T_{rot} = 5800$ K ± 500 K. The energy efficiency and conversion efficiency are observed to depend on flow and power.

Keywords: Microwave, CO_2, thermal plasma, CO_2 dissociation, atmospheric pressure

1. Introduction

The transition of the energy production technology from carbon-based fuels to renewable energy requires on demand energy storage and energy transportation. The power to molecule technology aims to store excess energy by conversion of molecules like CO_2 or CH_4 into chemical fuels.

The first step of a more complex chain that would lead to fuel synthesis consists in the dissociation of CO_2 into CO. Microwave plasmas have been investigated as possible means of CO_2 conversion [1]. Plasma has the promise of combining the advantages of fast response to the grid power oscillation with a promising energy and conversion efficiencies (up to 80 % and up to 80 % respectively, but not simultaneously) at reduced pressure [2]. Atmospheric pressure operation is preferred in order to increase the energy efficiency of the complete CO_2 transformation process, without using extra energy to work at reduced pressure.

The mechanism proposed in literature to achieve energy efficiency above 50 % is the dissociation of CO_2 via vibrational excitation [2]. In order to minimize the losses of vibrational excitation, a gas temperature below 3000 K is required [3]. Pulsed operation can be used to reduce the gas heating and therefore minimize the energy losses that are not actively used to dissociate CO_2. In this work a 2.45 GHz microwave CO_2 atmospheric pressure plasma will be studied and the effect of pulsing the microwave on the plasma will be discussed.

2. Experimental setup

The plasma torch used in this work has been modified from the original design of University of Stuttgart [4] and is capable of igniting the plasma at variable pressures. The torch is shown in figure 1 and consists of a cylindrical TE_{01} cavity and a coaxial resonator, a quartz tube of 30 mm outer diameter and 26 mm inner diameter which is mounted in the centre of the cylindrical resonator. The coaxial resonator placed at the bottom of the quartz tube serves to ignite the plasma at atmospheric pressure. The plasma is confined in the quartz tube. The 2.45 GHz microwave are generated by a magnetron MH3000S-213BB powered by a 3 kW power supply ML3000D-111TC, both are Muegge components.

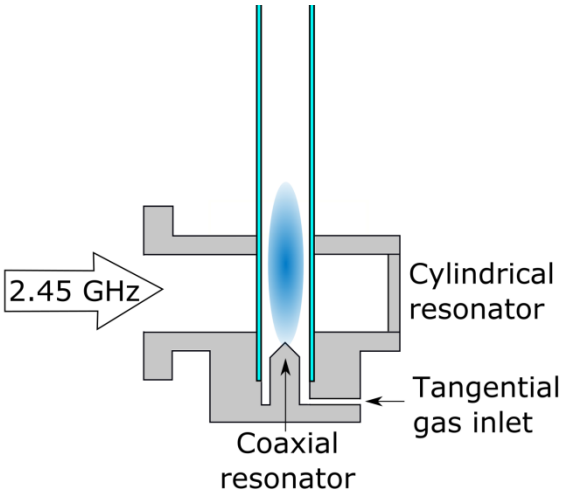

Fig. 1. Plasma torch setup.

The cylindrical cavity has 3 vertical slits of width 5.5 mm and height 43 mm (that corresponds to the cylindrical resonator height) these allow optical access to the plasma in the resonator. At the bottom of the coaxial resonator the gas is injected in the quartz tube by four tangential gas inlets. The end of the quartz tube is connected to a double wall pipe cooled by room temperature water. The plasma effluent is pumped away by a vacuum pump with variable pumping speed. The system is operated at atmospheric

pressure, with a gas flow between 10 slm up to 100 slm. The power supply can be operated in continuous or pulsed mode (500 Hz - 18 kHz) with a microwave power output that ranges between 300 W and 3000 W.
The energy efficiency and conversion efficiency, and their evolution with the plasma parameters such as flow and power, are quantified. The energy and conversion efficiencies are determined by analysing the gas composition as:

$$\alpha = 1 - \frac{[CO_2]^{out}}{[CO_2]^{in}} \quad (1)$$

$$\eta = \alpha \frac{\Delta H}{SEI} \quad (2)$$

where α is the conversion efficiency, [CO_2] stands for the carbon dioxide molar flow. The label "in" indicates the CO_2 injected in the system, while the label "out" the measured CO_2 in the plasma effluent. η is the energy efficiency ΔH the enthalpy of the CO_2 dissociation (2.9 eV) and the SEI is the specific energy input calculated as:

$$SEI = 0.0138 \frac{power[W]}{flow[slm]} \left[\frac{eV}{molecule}\right] \quad (3)$$

where the power is expressed in Watt and the flow in standard litre per minute. The system has two connections to the plasma effluent: the first connection is placed at 20 cm from the microwave cavity, the second at 2 m distance. The plasma effluent is sampled with a 0.9 mm diameter tube and analysed with a mass spectrometer. To reduce the pressure from atmospheric to the mass spectrometer working pressure (10^{-6} mbar) two orifices are used. A 100 µm orifice connects the 0.9 mm sampling tube with an intermediate chamber. This is connected to the ionization chamber of the mass spectrometer via a variable orifice. In this work the gas is sampled at two meters distance from the resonator to ensure that the gas mixture is uniform and that there is no gas separation due to the swirling flow.
The determination of the gas composition has been carried out by calculating a synthetic mass spectrum and using a least square minimization (python library scypy.optimize method L-BFGS-B) on the experimental data in order to determine the particle concentration in the gas [5]. A synthetic mass spectrum has been calculated as:

$$I(m) = \sum_i \beta_i n_i c_i^m(i) \quad (4)$$

where *I(m)* is the peak intensity at mass *m*, n_i is the species relative density of species *i* and c_i^m is the contribution (cracking pattern) to mass *m* of the species *i*.
Optical emission spectroscopy (OES) spatially (≈1 mm resolution) and temporarily resolved (≈500 ns resolution) is performed on the plasma in the resonator with the aim of studying the rotational and vibrational temperature of the emitting species in the plasma. Time integrated measurements are performed with a SPEX-1000 spectrometer (1800 l/mm grating) equipped with an ANDOR AK420-OE CCD camera, the latter has been absolutely calibrated between 240 nm and 840 nm with an Ulbricht sphere and a D_2 lamp. The observed emission spectra at atmospheric pressure consist of the C_2 Swan band ($d^3\prod_g \rightarrow a^3\prod_u$) along with the typical C (lines at 248 nm and above 900 nm) and O (777 nm and 844nm) lines. N_2 is added to the CO_2 plasma in order to produce CN and measure its emission: the violet band ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$). The analysis of the CN emission is used to benchmark the analysis of the C_2 Swan band. To determine rotational and vibrational temperature of the C_2 ($d^3\prod_g$) state and CN ($B^2\Sigma^+$) state, the molecular bands are fitted with synthetic spectra obtained under the assumption of Boltzmann distribution by using the program MassiveOES [6] in combination with the C_2 and CN lines databases [7,8].
Time resolved measurements are performed with an ANDOR Shamrock SR-i303 spectrometer (1200 l/mm grating) equipped with an ICCD camera iDUS 340T.
Imaging of the plasma is performed using the ICCD camera mentioned beforehand with the aim of determining the plasma volume. Both the plasma length and radial extension are studied.

3. Measurements and results

3.1 Continuous operation

The gas flow as well as the microwave power has been varied between 10 slm and 100 slm and between 900 W and 3000 W respectively. Below 900 W the plasma cannot be sustained.
The typical C_2 emission between 450 nm and 560 nm and its fit are show in Figure 2. The present spectrum has been obtained at 900 W, 10 slm CO_2 flow: the analysis of the C_2 emission gives T_{rot}= 5700 K ± 500 K and T_{vib}=5900 K ± 500 K. The CN Violet band analysis (performed with an additional flow of 0.3 slm of N_2 to the CO_2 flow) gives T_{rot}= 6000 K ± 500 K and T_{vib}=6000 K ± 500 K.

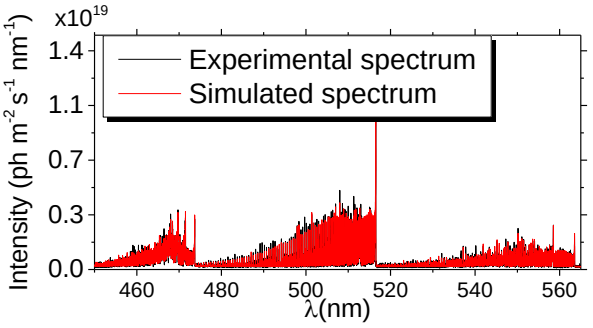

Fig 2. Typical emission from the C_2 Swan band, data obtained at 900 W power and 10 slm CO_2 flow.

The rotational and vibrational temperatures calculated from the C_2 ($d^3\prod_g$) state emission are constant in the studied conditions (flow between 10 and 100 slm, power between 900 W and 2700 W) with

$T_{vib} \approx T_{rot}$= 5700 K ± 500 K. The vibrational and rotational temperatures calculated from the C_2 ($d^3\prod_g$) state emission are compared with the ones calculated from CN ($B^2\Sigma^+$ state) emission, and found to be equal within the error bars.

At every power and flow studied, it was found that $T_{vib}(CN) \approx T_{rot}(CN) \approx T_{vib}(C_2) \approx T_{rot}(C_2)$ = 5800 K ± 500 K. The equilibrium between rotational and vibrational temperatures in the plasma suggests that the heavy particles in the plasma are internally in equilibrium.

Spatially resolved OES shows that the rotational and vibrational temperatures are constant along the vertical and radial directions of the resonator with $T_{vib} \approx T_{rot}$ = 5800 K ± 500 K. . Radial measurements show that the plasma is constrained in the centre of the quartz tube. Thus the rotational temperature calculated from the plasma emission is representative of the conditions in the centre of the quartz tube.

The conversion efficiency and energy efficiency have been measured at specific energy input between 0.1 eV/molecule and 3.7 eV/molecule. At flows above 40 slm the specific energy input could not be increased above 0.7 eV/molecule, thus the conversion efficiency never exceed 4 %, while the energy efficiency is between 16 and 21%. At lower flows the conversion efficiency increases up to 12%, but the energy efficiency decreases. The measured energy efficiency and conversion efficiency are found to be lower than the ones measured in other microwave plasma at reduced pressure [9]. This is consistent with the expectations: increasing the pressure reduce the energy and conversion efficiencies [2]. An example of conversion rate and energy efficiency measured at gas flow of 20 slm as a function of the power is shown in figure 3. The conversion efficiency increases with the power, while the energy efficiency constantly decreases, as typically observed [9].

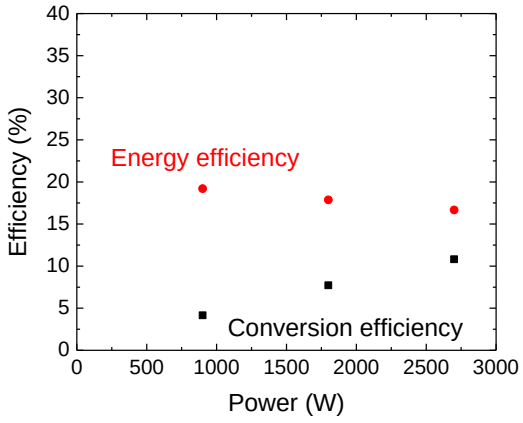

Fig 3. Energy efficiency and conversion efficiency measured at atmospheric pressure and 20 slm CO_2 flow.

In order to study the limiting factors of the conversion efficiency, ICCD imaging is performed. The measurements show that the plasma is confined in the centre of the quartz tube, typical the plasma diameter is less than a cm, and the length of the plasma in the vertical dimension increases with the power. The plasma is constrained by the swirling gas flow in the centre of the quartz tube. As the plasma length increases the volume increases as well. Thus the conversion efficiency can be correlated with the plasma volume. The plasma occupies always a small fraction of the quartz tube volume. This suggests that the CO_2 conversion is limited by the number of particles that cross the plasma region.

3.2 Pulsed operation

In order to compare continuous operation with pulsed operation the CO_2 plasma has been pulsed and time resolved measurements are performed. The measurements in pulsed mode focus on the C_2 ($d^3\prod_g$) state emission between 480 nm and 517 nm.

The development of the C_2 ($d^3\prod_g$) state rotational temperature during the pulsed is measured and is assumed to be the gas temperature as concluded in the steady state operation. Since the spectrometer used for pulsed measurements is only relatively calibrated, the fitted density value is only proportional to the real density. To avoid misunderstanding it will be called intensity.

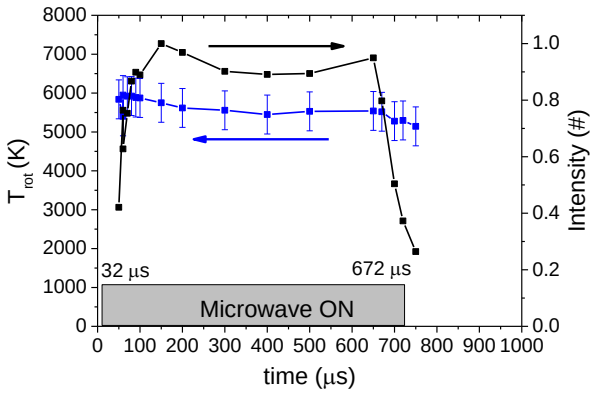

Fig 4. Typical C_2 rotational temperature (in blue) and intensity (in black) behaviour during a pulse. Data acquired at peak power 2700 W, with 20 slm CO_2 flow. Pulse frequency 1 kHz with a duty cycle of 65%.

Figure 4 shows an example of the C_2 rotational temperature and intensity behaviour during a pulse. The measurements are performed at atmospheric pressure with a CO_2 flow of 20 slm, the pulse frequency was 1 kHz with a duty cycle of 65%, the minimum achievable at this condition. The peak microwave power is 2700 W and the average power calculated as Duty Cycle*peak power is 1750 W, where duty cycle is the ratio between on and off time of the microwave. The measurements show that the rotational temperature is between 6000 K and 5500K during the pulse and it can be observed to decrease in the afterglow. The estimated cooling rate during the plasma afterglow is about 10^6 K/s. The C_2 ($d^3\prod_g$) state is observed directly at same value measured in steady state

after 50 μs from the beginning of the pulse. The intensity increases until 100μs and then is constant for the whole duty cycle. The trends observed in figure 4 suggest that the pulsing the microwave does not affect the plasma equilibrium that is reached in less than 100 μs. The C_2 intensity is fitted with a bounded exponential growth (until 600 μs) and an exponential decay (after 670 μs). Both functions describe well the behaviour of the intensity during the pulse. The characteristic grow time is 12 μs ± 1μs, while the characteristic decay time is 60 μs ± 11μs. The latter indicates that the C_2 ($d^3\prod_g$ state) is produced also when microwave are off, since the radiative lifetime of the C_2 ($d^3\prod_g$ state) is about 100 ns [6]. When the plasma is pulsed the same conditions observed in continuous operation are reached in few μs. This is corroborated by the typical conversion efficiency, which is found to be comparable to the ones obtained in steady state, with the same flow and average power.

4. Conclusions

In a CO_2 atmospheric pressure microwave plasma in continuous operation (at power between 900 W and 2700 W and flow between 10 and 100 slm) the rotational and vibrational temperature calculated from C_2 ($d^3\prod_g$) state and CN ($B^2\Sigma^+$) state emission are constant and equal within error-bars. It is suggested that the heavy particle in the plasma are described by $T_{rot} = T_{vib} = 5800$ K ± 500 K. The conversion efficiency and energy efficiency are below the expected values for thermal plasma. More studies are needed to identify the limiting factor for the conversion of CO_2.

In pulsed operation the rotational temperature measured from the C_2 ($d^3\prod_g$) state emission is observed directly at a temperature of 5800K ± 500 K after 50 μs from the beginning of the pulse. The energy efficiency and conversion efficiency measured in the pulsed CO_2 coincide with the values measured with the same average power and flow in continuous mode.

In order to achieve lower gas temperature future studies will be carried out to reduce the duty cycle of the pulse. To further improve the understanding of the plasma torch performance, gas dynamics simulation should be performed to investigate the interaction between the injected gas and the plasma in the torch.

5. References

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