Performance analysis of a 2.45 GHz microwave plasma torch for CO$_2$ decomposition in gas swirl configuration

F A D’Isa$^1$, E A D Carbone$^{1,3}$, A Hecimovic$^1$ and U Fantz$^1$

Max Planck Institute for Plasma Physics, Boltzmannstr. 2, 85748 Garching, Germany

E-mail: federico.disa@ipp.mpg.de and emile.carbone@ipp.mpg.de

Received 31 January 2020, revised 24 June 2020
Accepted for publication 29 July 2020
Published 16 October 2020

Abstract

Microwave plasmas are a promising technology for energy-efficient CO$_2$ valorization via conversion of CO$_2$ into CO and O$_2$ using renewable energies. A 2.45 GHz microwave plasma torch with swirling CO$_2$ gas flow is studied in a large pressure (20–1000 mbar) and flow (1–100 L min$^{-1}$) range. Two different modes of the plasma torch, depending on the operating pressure and microwave input power, are described: at pressures below 120 mbar the plasma fills most of the plasma torch volume whereas at pressures of about 120 mbar an abrupt contraction of the plasma in the center of the resonator is observed along with an increase of the gas temperature from 3000 K to 6000 K. The CO outflow is generally found to be proportional to the plasma effective power and exhibits no significant dependence on the actual CO$_2$ flow injected into the reactor but only on the input power at certain pressure. Thermal dissociation calculations show that, even at the lowest pressures of this study, the observed conversion and energy efficiency are compatible with a thermal dissociation mechanism.

Keywords: CO$_2$ valorization, energy storage, CO$_2$ plasma, microwave plasma, thermodynamics, mass spectrometry, power to molecule

(Some figures may appear in colour only in the online journal)

1. Introduction

Carbon dioxide, a highly potent greenhouse gas, is produced in very large quantities from industrial processes but also for power generation. In May 2013, its concentration in the atmosphere exceeded 400 ppm in the atmosphere for the first time in modern history [1] which should be compared to the 280 ppm that characterized conditions before the industrial revolution [2]. For achieving a target of 2 °C maximum increase of earth global warming, a complete decarbonization of the energy sector will be required by 2060 while scenario with maximum temperature of 1.5 °C will require negative emission [3].

Nowadays, the carbon dioxide emitted during electricity generation is contributing to about 20% of anthropogenic emissions totalling 30 000 Mt/y [4] both from fossil and also biogenic raw materials. CO$_2$ is not currently consumed in large quantities by the industry (in 2011, it averaged to a mere 150 Mt/y worldwide) and generally it is treated as a disposable waste. In this perspective several strategies to increase the usage of CO$_2$ are being investigated [5]. Additionally, renewable energy sources suffer from intermittency and a significant geographical mismatch between availability and demand. Energy storage and transport are necessary to stabilize the power grid and match the consumers demand. Several groups around the world have proposed CO$_2$ as a primary building block for synthesis of synthetic fuels such as methanol [6]. CO$_2$ re-use for energy storage is an attractive option for a zero-emission carbon cycle while solving the issues of intermittency of renewable energies and their transport to remote locations.

---

1 Authors to whom any correspondence should be addressed.

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
locations. CO\textsubscript{2} can be used as raw material and building block for the production of CO and thereafter synthetic fuels [7]. The current CO\textsubscript{2} valorization research focus mainly on electrocatalytic processes and thermochemical processes [8]. More recently non-equilibrium plasmas attracted interest as possible means of CO\textsubscript{2} conversion, especially for energy storage purposes [9]. Plasma devices offer high flexibility in terms of response times and scalability.

There are different types of plasma discharges used for CO\textsubscript{2} conversion: dielectric barrier discharge, microwave discharges, radio-frequency discharges, corona discharges, gliding arc discharges, and nanosecond pulsed high voltage discharges. A comprehensive overview of the different devices used for CO\textsubscript{2} decomposition has been given by Snoeckx and Bogaerts [10]. Typically, DBD discharges have a maximum energy efficiency of 20\% and a CO\textsubscript{2} conversion of about 40\%. With gliding arcs on the other hand energy efficiency up to 60\% have been reported but with conversion typically limited to a maximum of 30\%. Microwave discharges and RF discharges are reported to achieve the highest conversion (up to 90\%) and energy efficiencies (up to 80\%), albeit not simultaneously [10]. Microwave discharges represent the most promising technology for plasma assisted CO\textsubscript{2} conversion.

The dissociation of the CO\textsubscript{2} molecule requires a minimum energy of 5.5 eV, needed to break a CO\textsubscript{2} bond, but in presence of atomic oxygen additional dissociation of CO\textsubscript{2} can be obtained from the reaction (2).

\[
\text{CO}_2 + M \rightarrow \text{CO} + \text{O} + M \quad \Delta H = 5.5 \text{ eV} \quad (1)
\]

\[
\text{CO}_2^+ + O \rightarrow \text{CO} + \text{O}_2 \quad \Delta H = 0.3 \text{ eV} \quad (2)
\]

The potential energy (2.6 eV) of the O atom produced in the first step (process (1)) is then not lost via its mutual recombination with another O atom to form an O\textsubscript{2} molecule via the reaction O + O + M \rightarrow O\textsubscript{2} + M where M is a third particle or a wall, but rather invested to produce an additional CO molecule. In the latter scenario, the minimum energy requirement for one CO molecule production decreases to 2.93 eV/molecule.

\[
\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \quad \Delta H = 2.93 \text{ eV} \quad (3)
\]

Thermodynamically, this reaction has a specific energy requirement of 2.93 eV per dissociated CO\textsubscript{2} molecule at 400 K and at atmospheric pressure. The difference between processes (3) and (1) is due to the potential energy difference of the O atom in its free or bonded state (i.e. O\textsubscript{2} molecule), which is equal to halve the energy needed for splitting the O\textsubscript{2} bond. To obtain a specific energy requirement of 2.93 eV/molecule, it is then critical that the O atom also reacts with another CO\textsubscript{2} molecule to form a second CO molecule so that the potential energy of the O atom is not lost.

In a plasma, the dissociation of CO\textsubscript{2} can be induced either by electron impact processes or by thermal dissociation. Thermal dissociation is the consequence of the shift of the chemical equilibrium due to a high gas temperature. Non-equilibrium plasmas (i.e. plasma with significantly lower gas temperatures compared to electron temperatures) can help to obtain energy efficiency higher than the one obtained by thermal dissociation of CO\textsubscript{2}, albeit with lower conversion rate. High energy electrons (>10 eV) can induce dissociation of the CO\textsubscript{2} molecule by exciting the molecule into a dissociative state [10]. The latter process requires overall more energy than the thermal dissociation, thus is unfavorable. Another electron driven process is the excitation of the asymmetric stretching of the CO\textsubscript{2} via several electron collision leading to the dissociation of the CO\textsubscript{2} molecule. This mechanism is typically proposed in literature to explain an energy efficiency above 50\% (thus higher than the thermal dissociation limit) [11]. However such process requires a low gas temperature since the higher the gas temperature the faster are the losses of vibrational excitation into gas heating [12].

Due to their intrinsic low electric fields and high average power densities, microwave plasmas allow the generation of molecular plasmas with relatively low electron temperatures but high vibrational temperatures that can favor vibrational excitation in place of direct dissociation mechanisms by electron impact. Values up to 80\% energy efficiency were reported by researchers from the Kurchatov Institute [13–14] and have not been reproduced in recent experiments. The maximum energy efficiency was observed at pressures around 200 mbar [15] and degraded at higher and lower pressures. Nowadays, two types of microwave sources are mainly used to investigate CO\textsubscript{2} dissociation: in 915 MHz sources values of energy efficiencies up to 50\% and conversion up to 80\% have been obtained, although not simultaneously [16]. Typically energy efficiency and conversion anti-correlates, an high value of conversion implies low energy efficiency and vice versa. In the 2.45 GHz sources an energy efficiency between few percent and 30\% is obtained [16–19]. Belov et al [17] investigated a 2.45 GHz microwave plasma torch in a pressure range between 200 mbar and 900 mbar, with variable flow injection geometry (i.e. direct, tangential and inverse), concluding that the flow dynamics strongly influences the overall CO\textsubscript{2} conversion. Recent work by van den Bekerom et al [18] have shown that most of the literature results do not outperform the best possible thermal efficiencies and that in microwave plasma thermal dissociation and the plasma volume (heated fraction) leads to much higher effective SEI locally in the plasma. Wolf et al [20] identified, in a similar device, a homogeneous mode and two contracted modes between 50 mbar and atmospheric pressure. The radius in the contracted regime was found to be equivalent of one skin depth by Wolf et al [21].

To the best of our knowledge, no setup has been investigated systematically in both large pressure and gas flow range. This work focuses on the characterization of a 2.45 GHz microwave plasma torch in a wide flow power and pressure range as means of CO\textsubscript{2} conversion into CO, focusing on correlating the observed energy efficiency and conversion with the gas temperature and the plasma volume.

2. Experimental setup

The plasma torch used in this work has been modified from the original design of University of Stuttgart [22] so that it can be operated at atmospheric pressure but also at lower pressures. The experimental setup used in this work is shown in...
Figure 1. Schematic of the plasma torch and its exhaust system. Figure (b) shows the modified setup to measure the axial integrated optical emission. The most important components are indicated in the scheme.

Figure 1(a), it consists of a cylindrical TE10 cavity and a coaxial resonator. The coaxial resonator placed at the bottom of the quartz tube consists of two elements: a λ/4 resonator and a tip in its center. The tip consists of two geometrical parts: a cylinder of height 12 mm with a diameter of 15 mm and a cone of 8 mm height with a base diameter of 15 mm. The tip can be adjusted in height to enhance the electric field at its top for a given microwave frequency [23]. The tip position has been adjusted to have an enhanced electric field at 2.45 GHz by using a network analyzer. The enhanced electric field allows ignition in the pressure range 10–1000 mbar. A quartz tube of 30 mm outer diameter and 26 mm inner diameter is mounted in the center of the cylindrical resonator as can be seen in figure 1(a). The quartz tube length can be varied from a minimum of ca 8 cm up to 40 cm, in this work a 40 cm has been used. The cylindrical cavity has three vertical slits of width 5.5 mm and height 43 mm (that corresponds to the cylindrical resonator height) which 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 of 4.3 mm diameter. The 2.45 GHz microwave are generated by a magnetron MH3000S-213BB powered by a 3 kW power supply ML3000D-111TC, both are Muegge GmbH components. The power supply can be operated with a microwave power output that ranges between 300 W and 3000 W. The plasma is ignited and confined in the quartz tube. The end of the quartz tube is connected to a 2 m long water cooled pipe. The plasma effluent is pumped away by a vacuum pump with variable pumping speed. The system is operated at pressure between 30 mbar and 1000 mbar with CO2 flow rate between 2 and 100 L min⁻¹. However a CO2 flow below 5 L min⁻¹ typically generate unstable plasma at pressure above 100 mbar. At pressure lower than 100 mbar to use a low CO2 flow typically result in quartz tube heating when a microwave power above 1 kW is coupled into the plasma. The present setup differs from the one used in the Differ Institute for the presence of the ignition pin [16]. Moreover excepted for the inlet gas velocity and a slightly different microwave frequency (2.4 GHz), that also implies differences in the size of the microwave components, the present setup is similar to the one described by Butylkin et al [15] for which energy efficiencies up to 80% were reported. The plasma obtained can be operated in a flow range between 5 and 100 L min⁻¹.

Figure 1(b) shows the modifications of the experimental setup for measuring the plasma emission integrated along the axial direction (i.e. gas stream direction) and determining its radial cross section: a CF40 cube is introduced on top of the plasma torch, the cube side that face the quartz tube is provided with a quartz Thorlabs window WG42012. A Thorlabs mirror PF20-03-01 reflects the emitted light that is than measured with an ANDOR iStar ICCD camera with 2048 × 512 pixels of 13 μm size and a squared intensifier of side 18 mm, equipped with a Nikon lens of 35 mm focal length.

Optical emission spectroscopy is performed on the light collected via a double iris system that reduces the collection area to about 1 mm². The collected light is analyzed using an SPEX-1000 spectrometer (with a 1800 lines mm⁻¹ grating) provided with an Andor AK420-OE CCD camera. The optics have been absolutely calibrated in the wavelength range in the range between 250 nm to 400 nm with a deuterium lamp and between 400 nm to 850 nm with an Ulbricht sphere.
η is the energy efficiency, \( \Delta H \) the enthalpy of the CO\(_2\) dissociation (2.93 eV), and SEI is the global specific energy input calculated as:

\[
\text{SEI} = 0.0138 \, \frac{\text{power[W]}}{\text{flow[L min}^{-1}]} \cdot \frac{\text{eV}}{\text{molecule}}
\]

where the power is expressed in watt and the flow in standard liter per minute, the overall constant has the proper units to obtain the SEI in eV/molecule [26]. The total flow is used to calculate SEI and not the one that effectively interact with the plasma.

3. Experimental results

3.1. CO\(_2\) conversion and energy efficiency

The capability of the plasma torch for converting CO\(_2\) into CO and its energy efficiency is measured in a wide pressure range using mass spectrometry. The source performance from 60 mbar to quasi-atmospheric pressure (i.e. 880–930 mbar; the precision was limited by mechanical precision of the regulation valve) is shown in figure 2. The energy efficiency and conversion are shown as function of the global specific energy input (cf equation (7)). The measurement of the CO\(_2\) conversion is known within ±1.6%, because of systematic errors in the calibration procedure and background subtraction. The error on the energy efficiency is obtained by propagating the uncertainty on the conversion:

\[
\sigma_\eta = \sigma_\chi \cdot \frac{\Delta H}{\text{SEI}}
\]
Figure 2. Energy efficiency (red dots) and conversion (black dots) as function of the SEI. Flow and power have been varied between 3 and 100 L min$^{-1}$ (depending on the pump capacity) and between 900 and 2700 W, respectively. The effect of CO$_2$ flow and power on the SEI is indicated by the arrows in figure (a).

[17]. They reported an increase of the energy efficiency while using larger gas flows. However it should be noted that the experimental setup used in this work is different from the one used by Belov et al [17], particularly in terms of plasma cross section (140 mm) and although a vortex injection configurations was use, its geometry is different from the one used in this work, these differences can be the origin of the discrepancy.

The conversion and energy efficiency are typically depending only on the SEI, but at quasi-atmospheric pressure with a CO$_2$ flow of 5 L min$^{-1}$ the observed conversion deviates from the trend observed at 10 L min$^{-1}$. The lower flow is (probably) the main responsible of the observed deviation, but the physical mechanism behind it is still unclear. Such a trend could also be present at lower pressures, but shifted to higher SEI values. The latter hypothesis is supported by figure 2(b) where the conversion is observed to saturate at SEI higher than ca 2 eV/molecule. Further investigation in this direction are needed. Nevertheless carrying out measurements at SEI above 4 eV/molecule at pressure above 200 mbar is challenging, because of limitation in the MW power (max 3000 W) and since the plasma is unstable at flows below 5 L min$^{-1}$ and pressures above 200 mbar.

The conversion of CO$_2$ into CO is investigated as function of the pressure at fixed flow and power and the results are shown in figures 3(a) and (b), respectively. A contraction of the plasma takes place (see section 3.3 for more details) at about 120 mbar with the exact pressure value depending on the power coupled to the plasma: at 750 W the plasma contracts at 180 mbar, at 1500 W at 120 mbar and at 2400 W at 110 mbar. In figure 3 the contraction pressure is indicated by vertical dashed lines. The amount of CO$_2$ dissociated increases until the plasma contracts. The energy efficiency before the plasma contraction increases rapidly with pressure, it reaches an optimum at pressures near the contraction and then stays constant at low power and decreases at higher power. Interestingly, there are no abrupt changes in the conversion at...
the transition between contracted and expanded regime which depends on pressure and power input, but not on the input flow. Such effect can be explained considering the flow dynamics in the plasma torch but also that the plasma, in this gas temperature range, acts mainly as a heat source. This will be discussed in section 4.2 in more detail. These observations are in agreement with Fridman overview and discussion of results from the Kurchatov Institute [11]. After the contraction takes place the conversion of CO2 reduces with increasing the pressure, with the trend of the higher the power the stronger is the reduction. The energy efficiency follows similar trend as conversion. Similar observations were carried out also by Wolf et al [27] who measured an energy efficiency and conversion comparable to the one shown in figure 3. Notably, in a comparable device, den Harder et al [28] observed the same trend, but with higher maximum energy efficiency (up to 48%). The reasons for the differences between those experiments are not clear.

3.2. Gas temperatures of the plasma

To get more insight into the mechanisms of CO2 dissociation inside the plasma, the gas temperature is studied by means of optical emission spectroscopy. Figure 4 shows a typical emission spectrum, recorded in the resonator, of the plasma operated in the contracted regime. It is dominated by the C2 Swan (d^3Π_g → a^3Π_u) bands (visible in the range between 460 nm and 570 nm) similarly to what has been previously observed [16, 29–31]. A broadband continuum emission extending in the range 300–700 nm is also always present. Such emission is typically (much) less intense than the C2 Swan band or the atomic lines, but its contribution can be distinguished in the baseline of high resolution spectra (see figure 5) or in low resolution spectra since the lower dispersion allows better signal to noise ratio. Its origin is attributed to recombination processes of oxygen atoms via O + O → O2 + hν and CO + O + M → CO2 + M + hν reactions [32]. We note that in the lifetime of the experiment there have not been any evidence of the formation of solid carbon compounds neither by visualization in the resonator and in the effluent nor accumulation in the oil of the pump. Moreover in absence of hydrogen the usual aggregation processes leading to nucleation the aggregation of carbon into grains cannot occur [33]. The formation of carbon compounds which may contribute to the continuous emission is therefore excluded. In addition to that, one can identify some typical carbon (248 nm) and oxygen (at 777 nm and 844 nm) neutral lines.

Figure 5 shows the typical emission in the expanded regime: the spectrum is dominated by the continuum emission, on top of which can be identified the CO Angstrom (B1Σ^+ → A1Π) bands. The atomic oxygen lines can be observed at 777 nm and 844 nm, but no atomic carbon lines are detected. In the expanded regime that is observed only at low pressures, no C2 Swan bands are observed.

The C2 Swan bands emission spectra are fitted with synthetic spectra calculated using massiveOES [34] in combination with a database of lines and transition probabilities from Brooke et al [35]. The fitted temperature assuming a Boltzmann distribution allows describing accurately the rotational and vibrational population distributions (i.e. no deviation from Boltzmann distributions is found) which can therefore be associated to the gas temperature of the plasma (see Carbone et al [36] for more details). The analysis of the C2 Swan band shows consistently a gas temperature of about 6000 K ± 500 K in the center of the quartz tube independently of plasma conditions in the contracted mode (see section 4.1 for a discussion on that point). In the investigation of optical emission of C2 in CO2 microwave plasma carried out by Carbone et al on the same plasma setup was shown that the measured rotational and vibrational temperatures are constant within error bars and equal to each other in the constricted regime with a
Figure 4. Typical emission spectra absolutely calibrated recorded at 920 mbar, 10 L min$^{-1}$ and 900 W. The emission was recorded in the center of the resonator. The spectra region between 460 nm and 567 nm (C$_2$ emission) has been multiplied by 10.

Figure 5. Typical emission spectra absolutely calibrated recorded at 60 mbar, 10 L min$^{-1}$ and 900 W. The emission was recorded in the center of the resonator.

Figure 6. (a) shows the temperature evolution and the line integrated population density of the C$_2$ (d$^3$Π$_u$) state in the radial direction, red and black dots, respectively. The measurements were performed at height of 58 mm from the resonator bottom. Figure (b) shows the temperature evolution and the population density of the C$_2$ (d$^3$Π$_u$) in the axial direction, red and black dots, respectively. The measurements are performed in the center of the quartz tube, $r = 0$. In both cases the CO$_2$ flow is 10 L min$^{-1}$, the pressure 920 ± 10 mbar. The analysis of the C$_2$ emission has been performed on the $\Delta \nu = 0$ transition group.

A parametric study was performed while varying the power between 900 W and 3 kW and using 5–100 L min$^{-1}$ input gas flow [36] (i.e. similar conditions as the one investigated in sections 3.1 and 3.3). Figures 6(a) and (b) show the typical gas temperature and line integrated particle density evolution along the plasma radial and axial direction at 920 mbar. The LOS area is ca L mm$^{-2}$ (see section 2). Since the double iris system is moved by a $\mu$m translator whose precision is much smaller than the LOS size, the precision on the measurement position is assumed to be ca ±0.5 mm. The measurements are performed with a CO$_2$ flow of 10 L min$^{-1}$, a pressure of 920 mbar and microwave power of 900 W. The radial analysis is performed at a fixed height of 58 mm, thus in the early effluent. The
axial measurements are taken along the axis of the quartz tube inside the microwave resonator. In both cases the gas temperature measured from the $C_2$ rotational population distribution is constant at about $6000 \pm 500$ K. The axial analysis shows that the $C_2$ emission peaks in the resonator upper part and decay in the effluent. The upward shift of the plasma in the resonator is probably due to a combination of effects related to the gas flow and the distribution of the electromagnetic field inside the cylindrical cavity. The radial scan shows that the hot region (where $C_2$ emits) occupies only a small portion of the quartz tube. This is in accordance with the measurements reported in section 3.3. No temperature gradient are measured in the radial direction but this can be explained by the fact that only a small region is probed. Indeed, the $C_2$ molecules emit only in the core of the plasma where the gas temperature is the highest. Formation process of $C_2$ involves carbon atoms (as discussed by Carbone et al [36]) that can form (thermally) only at temperature above ca $5000$ K (see section 4.1). Groen et al [37] reported similar values and profile by O line Doppler broadening measurements in a pure CO$_2$ microwave discharge in constricted regime.

In the expanded regime, the emission spectrum is dominated by the CO (B$^1\Sigma^- \rightarrow A^1\Pi$) Angstrom bands. Silva et al [38] and Du et al [39] investigated the use of CO Angstrom bands as a thermometric species in CO$_2$ plasmas. They observed that the CO(B$^1\Sigma^-$) state rotational distribution, determined from the analysis of the $0-1$ vibrational transition, is in equilibrium with the surrounding gas temperature. Based on these studies, the rotational temperature of the CO(B$^1\Sigma^-$) state is used here also as a measure of the gas temperature. The CO rotational temperature is calculated using PGOPHER and the molecular constants from [47–50].

Figure 7 shows the measured gas temperature determined from CO(B$^1\Sigma^+$) and $C_2(d^3\Pi_g)$ emission spectra as a function of pressure. The measurements are performed between 60 and 1000 mbar in the middle of the resonator (+20 mm from the resonator bottom, radially centered $r = 0$). The measurement of the $C_2$ Swan band are carried out at constant CO$_2$ flow of 10 L min$^{-1}$ and microwave power of 900 W. The emission of the CO molecule is investigated for two conditions: CO$_2$ flow 5 L min$^{-1}$ and microwave power of 900 W and CO$_2$ flow of 10 L min$^{-1}$ and microwave power 1500 W. In the expanded regime the gas temperature is about $2400$ K $\pm$ $200$ K at 60 mbar and increases with pressure up to $2800$ K $\pm$ $280$ K.

Right before the transition from expanded to contracted regime, the measured gas temperature is $2800$ K $\pm$ $280$ K at a pressure of 125 mbar. Such measurement is consistent with the values measured by means of Raman scattering at the center of a similar plasma torch by van den Bekerom et al [18], while Wolf et al [20] measured an higher gas temperature at comparable discharge conditions. In the pressure range that operates in contracted regime (from ca 120 mbar up to 1000 mbar) similar gas temperatures values have been already measured by Babou et al [31], Spencer and Gallimore [30], Mitsingas et al [29], Bongers et al [16], Groen et al [37] and Wolf et al [20]. The vibrational temperature of the $C_2(d^3\Pi_g)$ state, in this study, is repeatedly observed to be in equilibrium with the gas temperature suggesting that the heavy particle in the plasma are in equilibrium, when the plasma is contracted. A vibrational temperature in equilibrium with the gas temperature is also measured by Babou et al [31] while Spencer and Gallimore [30] and Mitsingas et al measure an higher vibrational temperature $7700$ K, Bongers et al [16] measured an even higher vibrational temperature $9000$ K. The reason for such differences in the vibrational can be related to the low sensitivity of the $C_2$ Swan band $\Delta \nu = 0$ transition to the vibrational temperature as discussed in Carbone et al [36], but also the need of higher resolution spectrometer [36].

To summarize the observation: the plasma transition from expanded to contracted regime is abrupt and the plasma appears to be stable also close to the contraction pressure (no oscillation can be observed). No intermediate temperature can be measured around the transition. The abrupt temperature variation is consistent with the abrupt change of plasma size and hence the abrupt change in power density. It should be mention that Wolf et al [20] observed an intermediate pressure plasma using oxygen broadening measurement. We do not observe such intermediate gas temperature values. However the pin used in this work to ignite the plasma may affect the transition between expanded and contracted regime, which is more abrupt with respect to what observed by Wolf et al [20].

3.3. Plasma size

The axial integrated light emission has been acquired by ICCD imaging using the experimental setup shown in figure 1(b). This measurement gives the cross section of the plasma in the radial direction. The analysis of the plasma emission cannot be analyzed using a single bi-dimensional Gaussian profile but rather using a sum of two bi-dimensional Gaussian profiles. However, the separation of the plasma emission into two components has no strong physical basis and their width follow similar behavior changing the power, the CO$_2$ flow and the pressure. To reduce the systematic errors in the determination
Figure 8. Radial extension of the plasma at 2400 W and 10 L min$^{-1}$ at pressure of 60, 80, 100, 110 mbar. The microwave waveguide is positioned at the right side of the picture.

of the plasma region, it has then been defined as the region in which the light intensity is above 15% of its maximum. This is sufficient, with a good signal to noise ratio, to identify the region where the C$_2$ molecule, in the contracted regime, and the CO, in the expanded regime, emit light. The gas temperature can be determined from the emission of these molecules, therefore the identified region corresponds to the region where the gas temperature is the one discussed in section 3.2. Since the energy of the MW is coupled to the electrons and transfer by collision to the heavy species [40], the presence of hot gas (i.e. emission from CO or C$_2$) is assumed to be a trace of the presence of electrons, thus of plasma. The C$_2$ emission, as well as the CO emission, are observed always along with the atomic oxygen emission, which was postulated to be representative of the electron density spatial profile by Wolf et al [20, 21]. Moreover the oxygen emission profile measured using a band pass filter (840 ± 5 nm) is found to be equal (within 5% of difference that varies without systematic trends) to the emission profile measured without filter. The emission intensity of the C$_2$ Swan band is much higher than the atomic oxygen lines emission, which allows to have a better signal to noise (i.e. the recombination continuum) ratio. Therefore measurements without filter, which includes both C$_2$ Swan band emission (or CO emission) and the atomic oxygen lines, are preferred.

Figure 8 shows a measurement of the axially integrated light emission performed with the ICCD camera performed at 10 L min$^{-1}$ of CO$_2$ injection and a microwave power of 2400 W and pressures range from 60 to 110 mbar. At pressure of 60 and 80 mbar (figures 8(a) and (b)) the plasma emission shows an hollow profile, whereas at pressure of 100 mbar the plasma emission peaks in the center of the quartz tube (figure 8(c)). The transition depends also on the power coupled to the plasma, at 60 mbar, the plasma emission peaks in the center of the quartz tube for any power below ca 1500 W. Similar observation were carried out by Wolf et al [20] by imaging the plasma laterally. Using the classification given by Wolf et al [20] the plasma observed at 60 and 80 mbar is homogeneous plasma, at 100 mbar an L-mode confined plasma and at 110 mbar an H-mode plasma (or hybrid a distinction is not possible).

After the transition to a contracted regime (i.e. filamentary plasma) the plasma cross section abruptly and drastically reduces: the plasma diameter changes from of about 20 mm in the expanded regime to values below 10 mm. Figure 9(a)
Figure 9. Figure (a) shows the changes in the plasma cross section at constant pressure above 900 mbar and different flows. Figure (b) shows the effect of the pressure on the plasma cross section.

Figure 10. Figure (a) shows a photo of the plasma burning in the microwave cavity. Axial ICCD images of the plasma at 10 L min\(^{-1}\) of CO\(_2\) flow, pressure of 60 mbar and microwave power of 2700 W (b), 200 mbar and 2700 W (c), quasi-atmospheric pressure 900 W (d) and 2700 W (e).

shows the changes of plasma diameter with power at different flows and constant pressure above 900 mbar. Figure 9(b) shows the changes of the plasma diameter with power at pressure of 200, 500 and 900 mbar for a constant flow of 20 L min\(^{-1}\). The cross section of the plasma weakly decreases while increasing the pressure. The dominant parameter that defines the plasma cross section, after the plasma contraction takes place, is the microwave power coupled into the plasma.

The plasma extension in the axial direction is recorded with the ICCD camera mounted on the side of the microwave resonator. In the resonator the light emission is limited by the slit size (5.5 mm). Figure 10(a) shows an optical picture of the plasma taken from the side in which the masking due the waveguide wall is visible. Similarly to the cross section, the plasma extension in the axial direction (plasma length) was determined as the region where the emission is above 15%
of its maximum. In figure 10, some typical radial integrated plasma optical emission profile are shown for different pairs of pressure and power. The plasma extends in the effluent at atmospheric pressure (see figures 10(d) and (e)) and at low power does not fill the bottom of the resonator (figure 10(c)). Reducing the pressure the plasma extends much less in the effluent, as can be seen while comparing figures 10(c) and (e). Figure 10(b) shows, on the other hand, that in the expanded regime the plasma fills the resonator without extending above it.

A study of the plasma length is performed and the results are summarized in figure 11. The plasma length as function of power and for several flows is reported in figure 11(a) for near atmospheric pressure conditions (i.e. about 900 mbar). The flow only weakly influences the plasma length while the plasma length significantly increases with power. Figure 11(b) shows the effect of the power at different pressures and constant flow 20 L min$^{-1}$. The plasma length strongly increases with pressure. In the investigated power range at 200 mbar the axial elongation is mostly not visible because the microwave waveguide edge covers the variation of plasma emission. At pressure below 200 mbar the axial elongation is mostly not visible because the microwave waveguide edge covers the variation of plasma emission. At pressure below 200 mbar the axial elongation is mostly not visible because the microwave waveguide edge covers the variation of plasma emission. At pressure below 200 mbar the axial elongation is mostly not visible because the microwave waveguide edge covers the variation of plasma emission. At pressure below 200 mbar the axial elongation is mostly not visible because the microwave waveguide edge covers the variation of plasma emission. At pressure below 200 mbar the axial elongation is mostly not visible because the microwave waveguide edge covers the variation of plasma emission.

The SEI used in section 3.1 is calculated on top of the total CO$_2$ flow and microwave power coupled into the plasma. The plasma emission can also be used as a measure of the plasma volume and define a region of gas swirling around a hot plasma core. In that case, the local SEI for the molecules entering the plasma region is significantly higher than the global SEI based on the total gas flow entering the quartz tube. For the present setup, the typical local specific energy input calculated, as suggested by van den Bekerom [18], as the global SEI divided by the fraction of volume occupied by the plasma is always (much) above 10 eV/molecule in the contracted regime. A SEI of ca 10 eV/molecule is circa the SEI required to reach at thermal equilibrium a gas temperature of 6000 K (value obtained using the thermal equilibrium calculation, see section 4.1). However the temperature does not exceed 6000 K, thus the power is dissipated (or coupled) to a larger amount of particles. This effect can be described as an effective flow through the power deposition volume. If the plasma expands the flow of particles entering into it increases. The linear increase of the diameter and length with power, correlates with an increase of plasma surface, thus of radial inflow. The plasma keeps constant the effective SEI (power/treated flow) rather than the power density (i.e. the local SEI). In this perspective the flow dynamics are critical to understand the CO$_2$ conversion in this microwave plasma torch. The plasma is the heat source that determines the flow dynamics and provide the energy (i.e. the heat) to dissociate the CO$_2$ gas. Further considerations about the gas flow dynamics will be done in section 4.2.

4. Discussion

4.1. Thermal equilibrium considerations

In addition to electron driven processes, the contribution of thermal conversion of CO$_2$ into CO needs to be considered when a gas temperature above 2000 K is measured. To evaluate the degree of CO$_2$ dissociation in the core of the plasma, thermal equilibrium calculations have been performed using the program CEA [41]. CEA calculates the thermal equilibrium composition at fix temperature and pressure minimizing the
Gibbs free energy. However it does not include the gas dynamics, the recombination or the temperature gradient. den Harder et al [28] have shown that the thermalization time of the mixture is in the order of few microsecond at temperature above 4000 K, thus much shorter than the global gas residence time in the reactor (a few ms for the total flow under the approximation of conservation of mass flux through the reactor). We note that re-circulation flow patterns may increase locally the residence time of cold particles while the hot gas coming out of the plasma will expand rapidly. This means that, in the contracted regime, for the fraction of CO2 heated in the plasma core (i.e. at 6000 K), the thermal equilibrium composition is representative of the gas composition. At gas temperature lower than 3000 K (thus lower pressure), the residence time is not sufficient long to ensure (theoretically) a complete thermalization. However the thermal calculation represents the maximum conversion that can be expected to be produced by thermal dissociation, whose importance in low pressure microwave plasma has been also discussed by van den Bekerom et al [18] The purpose of this calculation is to serve as starting point to evaluate the impact of thermal dissociation onto the CO2 conversion, rather than predictive modelling of the CO2 conversion.

To understand the variation of chemical composition as function of the temperature in the investigated pressure range (60 mbar—quasi atmospheric pressure), the thermal equilibrium has been computed at several combinations of pressure and temperature. Figure 12 shows the molar fractions of CO2, CO, O2, O and C as a function of gas temperature while heating up a pure CO2 gas. The molar fraction of CO2 decreases rapidly above temperatures of about 3000 K with formation of CO and O2. Above this temperature O2 dissociate and the gas becomes a mixture of C and O atoms. It is then no coincidence to see that C2 Swan bands appearance is correlated with gas temperatures of about 6000 K, as recombination processes of C atoms lead to the formation of the C2 Swan bands in CO2 plasmas [36].

Figure 13(a) shows the degree of conversion of CO2 into CO as function of the gas temperature for different given pressures. Note that the conversion is calculated under the assumption that all the carbon atoms (that are formed at $T_{\text{gas}} > 5500$ K) recombine into CO. The pressure has only a weak effect on the conversion. For instance from 50 to 1000 mbar, the gas temperature required to convert 50% of the CO2 into CO increases from 2700 to 3050 K.

The calculated conversion refers to the CO2 dissociation fraction. The energy spend to heat the CO2 and used in the conversion of CO2 into CO can be expressed as (9):

$$Q = \int_{T_0}^{T_{\text{fin}}} (\frac{\partial H}{\partial T})_p \, dT = H(T_{\text{fin}}) - H(T_0)$$

where $T_0$ and $T_{\text{fin}}$ represent the initial temperature (298 K) and the final temperature, $H$ is the enthalpy of the gas mixture at a given temperature. The enthalpy of the mixture is a result of the CEA calculation, from which the energy per molecule required to obtain a given temperature can be calculated:

$$\text{SEI} = \frac{Q(J \cdot g^{-1}) \cdot 44.07\text{[g mol}^{-1}]\text{]}{e[J \cdot eV^{-1}]N_A[\text{molecule} \cdot \text{mol}^{-1}]\text{]}\text{]}$$

where $Q$ is given in J g$^{-1}$, 44.07 is the molar mass of CO2, $N_A$ the Avogadro number and $e$ the conversion factor between J and eV, hence the units of the SEI are eV/molecule. The latter is used to calculate the energy efficiency shown in figure 13(b). The energy efficiency of thermal dissociation of CO2 into CO is shown in figure 13(b) for the same parameters. The energy efficiency of thermal dissociation for producing CO peaks at about 3000 K and degrades at higher temperatures where energy is then spent not only for warming up the gas (i.e. via its heat capacity) but also for dissociating O2 and CO (see figure 12).

With the help of the thermal equilibrium calculation it is possible to investigate the importance of thermal dissociation in the measured conversion.

The gas temperature measured at 60 mbar in the microwave resonator is ca 2500 K, where a CO2 conversion of 30% is expected by thermal dissociation only. The maximum measured conversion rate at 60 mbar for the present setup is however only 25% (see figure 3). The lower measured conversion can be related to the gas temperature gradient, since not all the gas is heated to the measured temperature, but part of it is colder, thus a lower conversion can be expected. However to observe in an experiment the dissociation fractions given by figure 13(a), the mixture composition needs to be quenched rapidly to avoid recombination of CO via:

$$\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}.$$  \hspace{1cm} (11)

In order to minimize the losses the gas needs to be cooled down very rapidly (faster than 10$^7$ K s$^{-1}$ [11]) while exiting the plasma volume, since the process described in equation (11) is temperature dependent, and the reaction rates is proportional to $e^{-\frac{1500}{T}}$ [42]. This process typically happens in the
Figure 13. Plot (a) shows the CO$_2$ dissociation fraction expected at a given pressure as function of the gas temperature, under the assumption of ideal quenching (no CO$_2$ losses) and recombination of carbon atoms into CO. Plot (b) shows the expected energy efficiency at a given pressure as function of the temperature.

The plasma itself, in the gas layer that surrounds the plasma and in the effluent as evidence by its chemiluminescence continuum reported in section 3.2. The increase of converted CO$_2$ with pressure that can be observed in figure 3(a) can be correlated with the observed increase of gas temperature that is measured with power for a non contracted plasma. As the pressure increases the gas temperature increases with a maximum of 2800 K measured experimentally right before the transition to a contracted regime. Assuming a thermally driven dissociation process, thermal calculations do predict an increasing energy efficiency with gas temperature as seen in figure 13(b). On the other hand the pressure has only a limited effect on the absolute value of the energy efficiency for thermal dissociation, the gas temperature has the stronger influence on energy efficiency. The observed increase in conversion with power has to be also compared with the plasma size and low overall conversion rate. Moreover a pressure increase at gas temperature below 3000 K (see figure 13(b)) would actually reduce (slightly) the energy efficiency, while an increase of energy efficiency is observed here (see figure 3(a)), indicating that the gas temperature effect would be the driving force of conversion. The highest energy efficiency is measured at ca 120 mbar (at the plasma contraction) in good agreement with previously reported trends by Kurchatov Institute, but with lower overall energy efficiencies [11]. The measured energy efficiencies are maximum 30% which is much lower than the 80% reported by Butylkin et al [15], where vibrational ladder climbing was identified as mechanism for CO$_2$ dissociation. The overall lower energy efficiency can be explained, by the dissociation mechanism, since in the present setup thermal dissociation is the dominant dissociation mechanism, thus the maximum energy efficiency is limited by the thermal dissociation efficiency. The known differences between the two setups are: the inlet gas velocity (ca 10$^3$ cm s$^{-1}$) reported by Butylkin et al [15] is higher than the one expected in the present setup (ca 10$^2$–10$^3$ cm s$^{-1}$), the tube has an inner diameter of 32 mm (compared to 26 mm in this work), the microwave frequency 2.4 GHz and the wave-guide components size. However if and how these geometrical differences influence the dissociation mechanism of CO$_2$ is not understood.

The plasma contraction increases significantly the power density, that drives an abrupt increase of the gas temperature which reaches a value of 6000 K ± 500 K and remains constant at every flow, power and pressure investigated. Thermal calculations predict at such high temperature that energy efficiency should increase with increasing pressure. The opposite trend is however found experimentally (see figure 3). Losses of CO by recombination via reaction (11) is a pressure depend process (via the third body collisional term in the rate coefficient). Even if locally the conversion of CO$_2$ into CO can be high, the recombination process reduces the CO molar fraction measured downstream of the plasma reactor. At low gas flow rates (i.e. high specific energy input as shown in figure 2), one can expect a slower cooling rate meaning that a larger fraction of CO is lost. A decrease of conversion and energy efficiency are indeed observed at low gas flows (<10 L min$^{-1}$) which is more pronounced at high pressure. Finally another effect should be taken in account, the plasma elongation in the effluent is correlated with an increase of microwave radiation field into the room (it has been measured using a microwave-power meter). This indicates the generation of a surface-wave: in the absence of a Faraday shield around the quartz tube, a surface wave discharge does not absorb all the power from the applicator and radiates part of its energy as an antenna [43]. Such effect would effectively reduce the power coupled to the plasma. If a lower power is coupled to the plasma the fraction...
of CO₂ converted reduces (as seen in figure 2) and the energy efficiency underestimated by overestimating the SEI.

In the contracted regime the plasma however occupies only a small part of the tube and hydrodynamic effect between the cold swirling gas flow and hot plasma core should be additionally considered (see below for more discussion).

4.2. Flow dynamics considerations

Following the assumption of local chemical equilibrium, the temperature profile in the quartz tube defines the region where CO₂ dissociation takes place. Babou et al. [31] showed that temperature gradients at the edge a N₂–CO₂ microwave plasma are relatively steep. Recently Wolf et al. [20] systematically investigated the temperature profile in the core of the plasma reaching similar conclusions. In first approximation we can assume, based on these observations, that the temperature gradients are strong, the non-emitting does not contribute significantly to the conversion. The conversion observed can be related to mixing between the cold gas and the hot gas driven by the temperature gradient. The amount of CO₂ that flows from the cold region into the (hot) plasma should then be proportional to the surface (or volume) of the hot region itself.

Figure 14 shows the CO₂ conversion fraction as a function of the ratio between plasma cross section and gas cross section in several experimental conditions. The plasma cross section is the one discussed in section 3.3, whereas the gas cross section is the cross section of the quartz tube from which the plasma cross section has been subtracted. The ratio between plasma and gas cross sections does not show any direct correlation with the conversion. Only at high flow a correlation can be found, which may be purely coincidental. It should be also noted that at 100 L min⁻¹ the plasma does not have any longer a cigar shape, but it is twisted by the strong swirl. These observations indicate that gas mixing dynamics at the edge of the plasma probably represent the key effect to understand the CO₂ conversion in the high pressure regime.

Figures 15(a) and (b) show the CO_out flow at 200 mbar as function of the power coupled into the plasma. Similar trend at 900 mbar is found for the 20, 40 and 100 L min⁻¹ conditions (figure 15) while for an input gas flow of 10 L min⁻¹ a reduction in CO_out flow is measured. Such reduction of conversion with pressure at the lowest flow appears at 500 mbar and quasi-atmospheric pressure as seen in figure 2. The CO_out flow appears to be only a function of the microwave power (that scales linearly with the plasma surface, see figures 9 and 11) and weakly influenced by the input CO₂ gas flow. The turbulent mixing that drives the CO₂ gas into the plasma is not depending on the magnitude of the CO₂ flow, thus it appears to be driven by the gas temperature gradient. The approximated temperature gradient (T_plasma - T_gas) is independent from the gas flow (see sections 3.2 and 3.3). This hypothesis is consistent with the observations carried out in sections 3.2 and 3.3: neither the plasma size nor the temperature are affected by the CO₂ input flow. As a result the influx of cold gas into the plasma region is the same, thus the total CO out flow is constant at given pressure and power. On the other hand a power variation changes the plasma dimensions (see section 3.3) and consequently the CO₂ flux into the plasma increases. A CO₂ conversion driven by the particles that flow radially to the plasma and the mixing of the hot plasma effluent with colder gas can also explain the lack of an abrupt change in conversion at the transition between expanded and contracted regime. The main difference between expanded and contracted regime is where the microwave power is coupled. The CO₂ dissociation is driven, close to the transition between expanded and contracted regime, by thermal processes (see figure 17). In this region the plasma act as an heat source and if the inflow does not change at the contraction the conversion is expected to follow. The reason why the gas flow is not strongly influenced by the contraction is not fully understood yet and requires additional investigations especially in the direction of flow modelling.

The increase of pressure leads to a significant increase in length of the plasma (see figure 11). The increase of CO₂ influx (due to the longer plasma) appears not to be sufficient to compensate for the higher recombination of CO into CO₂ (reaction 11) that is expected to increase at higher pressure. At low gas flow and high pressure, where a decrease of conversion is observed at increasing powers (see figures 2(a) and 15(b)), the decrease in energy efficiency is then (probably) related to the gas flow dynamics, both in terms of mixing but also heating of the effluent (due to a combination of longer plasma and lower amount of cold CO₂ gas reservoir) that causes higher recombination of CO into CO₂. The present considerations can then only serve as a basis for a detailed modelling of the plasma and gas flow interactions, while focusing on understanding the impact of the plasma size on the flow dynamics. The investigation of the CO out flow allows the conclusion that the amount of CO produced in the setup used in this work is determined by the pressure and the ratio between power coupled into the plasma.

Wolf et al [21] found that the plasma size is skin depth limited, therefore it is expected to be independent from the quartz tube diameter and to only depend of parameters such
as microwave frequency and electron density. It can therefore be expected that the fraction of CO$_2$ gas that interacts with the plasma can be increased by reducing the quartz tube size, since the plasma would fill a larger fraction of the quartz tube. Similarly with lower inlet gas velocities, residence times of the gas in the plasma reactor increase. However Butylkin et al [15] obtained higher energy efficiencies and conversion rates for the same SEI and power inputs using a larger tube and higher tangential gas velocities for the gas inlet. Interestingly, the highest energy efficiencies reported by Bongers et al [16] were reported for a tube diameter of 30 mm with only one gas inlet. For any given gas flow, lower number of gas inlets and smaller inlet diameters will correspond to higher swirl numbers (i.e. ratio between tangential and axial velocities). The turbulent mixing in a swirl flow with a heat source is quite complex but it is known that higher swirl numbers correlate with larger pressure and density radial gradients [44]. Intuitively, higher inlet gas velocities would correlate to shorter residence times in the plasma and potentially more efficient gas cooling. For the present plasma torch, increasing the gas flow by a factor 10 does not change the gas temperature at all as discussed in section 3.2. About the mixing rate between the hot plasma core and the cold (swirling) gas layer there are only indirect information. The present study indicates that there is no direct correlation between the ratio of the cross sections of the plasma and of the tube with conversion efficiencies. Such correlation is expected if axial velocities (and consequently residence times) play a determining role in the plasma and gas flow dynamics. The observation that the highest energy efficiencies are measured in discharges with larger tube diameter (and higher gas inlet velocities) can tentatively be correlated to an enhanced stability of the vortex with a stronger particle densities gradients, effectively increasing the fraction of CO$_2$ converted. The possibility of improving the gas mixing by increasing the inlets velocity (at fixed total flow) and varying the quartz tube diameter needs further investigations.

4.3. Impact of electron driven processes on CO$_2$ dissociation

An analysis of the C$_2$(d$^3\Pi_g$) molecule rovibrational distribution functions, performed by Carbone et al in the same setup [36], showed that its rotational and vibrational states are in equilibrium with the gas temperature. The measured temperatures allow describing the conversion rates of CO$_2$ into CO satisfactorily by invoking a combination of thermal dissociation and flow dynamics. Pietanza et al [45] performed calculations of the electron energy distribution function (EEDF) in CO$_2$ microwave plasmas while taking into account superelastic processes. They showed that at reduced electric fields typical for microwave discharges that electron are in non-equilibrium with vibrational distribution function of CO$_2$. Recent plasma impedance simulations carried out by Groen et al [37] predict, that in the expanded regime (i.e. at $p < 125$ mbar), the electron temperature ranges between 2 and 3 eV. On the other hand, in the contracted regime the electron temperature may vary between 0.5 and 1 eV. Such investigations suggest that the plasma generated in the plasma torch is not in thermal equilibrium. The electron impact processes are typically (although those are not the only processes) responsible for the formation of both atomic and molecular electronically excited species. In addition to rotational and vibrational states densities, the density of electronic states density can be determined by absolute calibrated optical emission spectroscopy. Plasma ground states species calculated using thermal equilibrium assumption and the gas temperature can be used as input for constructing a Boltzmann plot. The density of these species can be correlated to the electron temperature and the EEDF. Knowing the density of the ground state, it is then possible to define an excitation temperature for that state that is related to the electron temperature. The electronic states are predominantly produced by electron impact processes. When the latter condition is not fulfilled (which is likely the case for C$_2$(d$^3\Pi_g$) state) no information of the EEDF can be obtained. Although this temperature is usually not the electron temperature, its value usually
Figure 16. Figure (a) shows the excitation temperature of the atomic carbon (black dots), atomic oxygen (red dots) and gas temperature (gray diamonds). Figure (b) the typical Boltzmann plot. The one shown here has been obtained at 10 L min$^{-1}$, atmospheric pressure and 900 W.

Figure 16 gives an indication of the latter with the electron temperature usually higher than the excitation temperature for ionizing plasma [46].

Figure 16(b) shows the typical Boltzmann plot that can be obtained by combining thermal equilibrium calculations and absolutely calibrated optical emission spectroscopy. The shown Boltzmann plot has been obtained at quasi-atmospheric pressure, 10 L min$^{-1}$ and 900 W. The fitting parameters are shown in figure 16(b). Figure 16(a) shows the excitation temperature for the measured electronic states of O and C atoms and the C$_2$(d$_3^3\Pi_g$) molecular state as function of the pressure. The transition considered are the C (3s$^1P \rightarrow 2p^1S$) and the O(3p $^5P_1,2,3 \rightarrow 2s^5S_2$), and O(3p $^3P_0,1,2 \rightarrow 3s^3S_1$). The data points obtained at pressures below 150 mbar are obtained in expanded regime, where no emission from C can be measured. Only the population of few states is known the several order of magnitude difference between the energy of the ground state and the excited states ensure that the excitation temperature is weakly influenced by the change of ground and excited state density. For example a factor 2 change in the oxygen ground state density changes the excitation temperature of less than 5%. However it should be considered that selective population (or depopulation) processes of the excited states can take place, which may lead to systematic errors on the calculated excitation temperature.

The C$_2$ excitation temperature cannot be used to get insight in the EEDF. In fact the C$_2$(d$_3^3\Pi_g$) state is the initial source term for the C$_2$ molecule via the reaction [36]:

$$\text{C} + \text{C} + \text{M} \rightarrow \text{C}_2(\text{d}_3^3\Pi_g) + \text{M}$$

The C$_2$ molecule is formed in its excited state as discussed in Carbone et al [36]. Therefore the C$_2$ excitation temperature is influenced by the formation mechanism and cannot be used to get information on the electron energy.

Based on the excitation temperature observed the plasma can be assumed to be is local thermal equilibrium in the contracted regime. Such electron temperatures are in relatively good agreement with calculations of Groen et al for the contracted regime [37]. A result that agrees also with the observation carried out by Babou et al [31], where the line ration method shows excitation temperature equals to the gas temperature.

At lower pressure the excitation temperature observed from the atomic oxygen emission is higher than the gas temperature indicating a non-equilibrium. However, there are no differences between the excitation temperature in the contracted and expanded regime. Assuming that this excitation temperature is representative of the electron temperature (at least in trend and not necessarily in absolute values), this result does not agree with predictions from Groen et al [37] who predicts an electron temperature between 1 and 3 eV, increasing from contracted to expanded regime. The reason behind such observation is not understood and should be further investigated. The interpretation of such excitation temperature should be supported by a collisional radiative model for the O atom electronic states. The present measurements are however still an indication that there is a non-equilibrium between the electrons and the neutrals in the expanded regime. Since the electron temperature in an ionizing plasma cannot be smaller than the one measured from the excitation temperature of electronic states (i.e. Boltzmann plot). One should also note that for the present microwave discharge the EEDF is non-Maxwellian and the so-called electron temperatures usually refers to 2/3 of the mean electron energy. In the case of recombining plasmas (i.e. electronic states are produced by recombination of ions--electron pairs) such statement is of course then not valid anymore and an electron temperature can be lower than the one deduced from a Boltzmann plot (see [46]). We also note the case of neutral collisional processes leading to production of radiative states such as the C$_2$ Swan bands. In such cases care should be taken while analyzing excitation temperatures (discussed above).
To assess the impact of electron driven process onto the CO$_2$ conversion, the measured conversion and energy efficiency are compared with the thermal limit. The latter is calculated using CEA program, thus it assumes that the CO$_2$ gas is heated homogeneously and without CO losses. Figure 17 show a comparison between the experimentally measured energy efficiency and conversion with the theoretical thermal conversion. The latter is calculated using the gas temperature and pressure of the experimental conditions. The calculated conversion (under the assumption that the measured gas temperature is representative of the one of the whole plasma core) represents an upper limit to the conversion that can be obtained from solely thermal dissociation. Indeed the recombination processes and the temperature gradients (but also the limited plasma volume) can only produce a reduction of CO$_2$ conversion in the experiments. Instead the thermal energy efficiency is meaningful only if all the CO$_2$ is converted at the measured gas temperature and there are no CO losses.

The conversion in the contracted regime is well below the thermal limit, which can be explained considering that not all the injected gas is heated to 6000 K. The conversion in the contracted regime is coherent with the thermal conversion expected down to ca 60 mbar. At lower pressures however the measured conversion is higher than the one expected from only thermal contribution and it is expected to increase at higher powers. Thus the observed conversion rates can be explained invoking only thermal conversion in the pressure range 60–1000 mbar. However at lower pressures the electron driven processes start to play a role, which are more relevant and easily identifiable at high specific energy input when the conversion rates exceed the thermal dissociation limit prescribed by the gas temperature.

The energy efficiency is always lower than the expected energy efficiency. Notably in the contracted regime the energy efficiency is consistent (in the lowest power case 750 W, see figure 3) with a CO$_2$ conversion taking place at 6000 K, without significant losses.

5. Conclusions

A 2.45 GHz microwave CO$_2$ plasma torch is characterized by means of OES, ICCD imaging and mass spectrometry in the pressure range between 20 mbar and quasi-atmospheric pressure (>900 mbar). At pressures below ca 120 mbar the plasma is observed to fill the tube while at higher pressures, the plasma contracts into a filament, occupying less than 10% of the quartz tube cross section. The pressure at which the contraction occurs varies between 110 mbar at 2400 W of input power and 170 mbar at 750 W of input power. The gas temperature increases from 2400 K up to 3000 K between 60 mbar and ca 110 mbar. At the contraction point, the gas temperature abruptly increases to 6000 K and remains constant at this value up to quasi-atmospheric pressure. For the gas temperatures reported in this study, the observed CO$_2$ conversion rates into CO can be explained solely while invoking thermal processes. Moreover the appearance of the C$_2$ Swan band is correlated with the formation of carbon atoms from CO dissociation that takes place thermally only at temperatures above 5000 K. The highest energy efficiency (ca 35%) is measured at ca 120 mbar concurrently with the plasma contraction.

In the contracted regime, the observed CO$_2$ conversion rates appear to be driven by the mixing between the cold gas and the hot gas. Indeed, the measured plasma cross section is not sufficient to explain alone the outflow of CO. At 200 mbar, it is found that the CO outflow is independent of the inlet CO$_2$ gas flow and that CO outflow scales with input power the latter is correlated to the surface of interactions between the plasma and the cold swirl gas flow and it increases with the power input. Near atmospheric pressure and at low gas flow rates, the conversion rate decreases with input power due to a...
combination of factors, i.e. swirl and plasma lengths but also gas cooling rates that may not be high enough as well as microwave leaks that can reduce the power coupled to the plasma. The excitation temperatures calculated from the population of the excited species of C, O and C2 indicate that the plasma is near thermal equilibrium in the contracted regime and effectively a non-equilibrium is obtained only at lower pressure, in the expanded regime. The measured conversion rates can be explained by considering only thermal dissociation and flow dynamics. Consequently non-equilibrium vibrational-ladder climbing leading to CO2 dissociation is not needed to explain the present results.

The gas flow dynamics play an important role in the investigated microwave setup. To improve the understanding of the CO2 conversion in the present configuration, detailed gas flow simulations are necessary. The present experimental results could allow a detailed benchmark of a plasma/gas flow self-consistent calculations in the future.

ORCID IDs
F A D’Isa https://orcid.org/0000-0002-2486-5602
E A D Carbone https://orcid.org/0000-0003-3455-0708
A Hecimovic https://orcid.org/0000-0002-3281-8507
U Fantz https://orcid.org/0000-0003-2239-3477

References
[1] Showstack R 2013 EOS Trans. Am. Geophys. Union 94 192
[2] Monastersky R 2013 Nat. News 497 15
[3] International Energy Agency 2017 Energy Technology Perspectives 2017 (France: IEA) https://doi.org/10.1787/energy tech-2017-en
[4] Aresta M et al 2013 J. CO2 Util. 3-4 65–73
[5] Quadralli E A et al 2011 ChemSusChem 4 1194–215
[6] Sherwin M and Blum D 1979 Liquid-Phase Methanol. Final Report Chem Systems Inc., Fairfield, NJ (USA)
[7] Ganesh I 2014 Renew. Sustain. Energy Rev. 31 221–57
[8] Schlögl R 2013 Chemical Energy Storage (Berlin: de Gruyter & Co) pp 1–34
[9] Bogaerts A and Neyts E C 2018 ACS Energy Lett. 3 1013–27
[10] Snoeck R and Bogaerts A 2017 Chem. Soc. Rev. 46 5805–63
[11] Fridman A 2008 Plasma Chemistry (Cambridge: Cambridge University Press)
[12] Azizov R I et al 1983 PhD 28 567
[13] Legasov V A et al 1978 Dokl. Akad. Nauk SSSR 238 66–9
Translation courtesy of Nikolay Britun
[14] Azizov R I et al 1983 Dokl. Akad. Nauk SSSR 271 94–8
Translation courtesy of Nikolay Britun
[15] Butylkin I P et al 1981 Zh. Tekh. Fiz. 51 925–31
[16] Bongers W et al 2017 Plasma Processes Polym. 14 e201600126
[17] Belov I et al 2018 J. CO2 Util. 24 386–97
[18] van den Bekerom D et al 2018 Plasma Sources Sci. Technol. 28 055015
[19] van Rooij G J et al 2015 Faraday Discuss. 183 233–48
[20] Wolf A J et al 2020 Plasma Sources Sci. Technol. 29 025005
[21] Wolf A J et al 2019 Plasma Sources Sci. Technol. 28 115022
[22] Leins M et al 2013 Contrib. Plasma Phys. 54 14–26
[23] Leins M 2010 PhD Thesis Fakultat Mathematik und Physik der Universitöt 40 Stuttgart
[24] Hecimovic A et al 2019 Rev. Sci. Instrum. submitted
[25] Drenik A et al 2017 Fusion Eng. Des. 124 239–43
[26] Britun N et al 2018 J. Phys. D: Appl. Phys. 51 144002
[27] Jan Wolf A 2020 PhD Thesis DIFFER
[28] den Harder N et al 2016 Plasma Processes Polym. 14 1600120
[29] Mitsingas C M et al 2016 IEEE Trans. Plasma Sci. 44 651–6
[30] Spencer L F and Gallimore A D 2012 Plasma Sources Sci. Technol. 22 015019
[31] Babou Y et al 2008 Plasma Sources Sci. Technol. 17 045010
[32] Peeters F et al 2019 ISPC 24 (Naples)
[33] Bundaleska N et al 2018 Phys. Chem. Chem. Phys. 20 13810–24
[34] Voráč J et al 2017 Plasma Sources Sci. Technol. 26 025010
[35] Brooke J S A et al 2013 J. Quant. Spectrosc. Radiat. Transfer 124 11–20
[36] Carbone E et al 2019 arXiv:1911.13121
[37] Groen P W C et al 2019 Plasma Sources Sci. Technol. 28 075016
[38] Silva T et al 2014 Opt. Lett. 39 6146
[39] Du Y et al 2017 Plasma Chem. Plasma Process. 37 29–41
[40] Schulz A et al 2012 Contrib. Plasma Phys. 52 607–14
[41] McBride B J and Gordon S 1996 Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications II Users Manual and Program Description NASA Lewis Research Center Cleveland, OH
[42] Tsang W and Hampson R F 1986 J. Phys. Chem. Ref. Data 15 1087–279
[43] Moisan M and Nowakowska H 2018 Plasma Sources Sci. Technol. 27 073001
[44] Vaidya H A et al 2011 J. Phys.: Conf. Ser. 318 062022
[45] Pietanza L D et al 2016 J. Phys. Chem. A 120 2614–28
[46] van der Mullen J A M 1990 Phys. Rep. 191 109–220
[47] Niu M L, Salumbides E J, Zhao D, de Oliveira N, Joyeux D, Nahon L, Field R W and Ubaechs W 2013 Mol. Phys. 111 63–2174
[48] Kepa R and Rytel M 1993 J. Phys. B: At. Mol. Opt. Phys. 26 3355
[49] Field R W, Wicke B G, Simmons J D and Tilford S G 1972 J. Mol. Spectrosc. 44 383–99
[50] le Floch A C and Amiot C 1985 Chem. Phys. 97 379–89