Enhancement of CO_2 conversion in microwave plasmas using a nozzle in the effluent

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Abstract. Plasma conversion is an alternative approach to the electrochemical and photochemical technologies searching for most efficient way to convert CO_2 into carbon monoxide (CO). The CO_2 plasma conversion investigated in recent years demonstrated conversion and energy efficiencies up to 50 %. Commonly, these values are obtained at pressures lower than atmospheric pressure at about 100 mbar. In this work we present an investigation of the CO_2 conversion and the energy efficiency in a microwave plasma torch equipped with a nozzle of different diameters installed downstream of the plasma at varying distances to the microwave discharge, in the pressure range 100-900 mbar. The results obtained using the nozzle demonstrate an enhancement of conversion and energy efficiency, particularly at pressures close to atmospheric pressure and for lower CO_2 flows (SEI above 2 eV/molecule), bringing the values of conversion and energy efficiency close to those obtained at lower pressures. It is assumed that the fast cooling of the hot plasma gas with surrounding colder gas leads to reduction of CO recombination into CO_2 thus preserving the maximum conversion obtained. With a 2.5 mm nozzle at sub-atmospheric pressures, conditions with large pressure difference in the resonator and in the effluent are observed, which is accompanied by an additional increase in conversion. A likely reason for this is reduction of the recombination rates due to lowering of the pressure in the effluent and possible temperature reduction resulting from the supersonic expansion. Using the nozzle it is possible to significantly increase the performance of the plasma torch at 900 mbar, both in conversion and energy efficiency towards values achieved at 200 mbar, which is an important step towards industrial applicability of this technology.

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1. Introduction

Plasma conversion is an alternative to the electrochemical and photochemical technologies searching for most efficient way to convert CO_2 into carbon monoxide (CO). Plasmas have certain advantages over electrochemical technologies, such as not relying on rare earth materials, flexibility in terms of short activation times (suitable for intermittent renewable energy), and easy scalability. Also, typical problems of electrochemical technologies such as long term performance due to degradation, are not expected to occur in a typical microwave plasma setup due to its robust design and lack of electrodes that would otherwise be prone to degradation, corrosion or contamination. On the other hand the CO_2 plasma conversion investigated in recent years demonstrated conversion and energy efficiencies up to 50 % [1, 2, 3, 4], compared to energy efficiency close to 100% of the solid oxide electrolysis [5].

The most successful type of plasma reactor reaching highest values of conversion and energy efficiency has proven to be a microwave plasma reactor operating in the pressure range between 1 and 1000 mbar [6]. In this pressure range, the plasmas exhibits two distinctive modes, diffusive and contracted mode. The diffuse mode appears at pressures around and below 100 mbar, with gas temperatures reaching up to 3000 K and conversion and energy efficiency up to 40-50%. With increasing pressure the plasma contracts, the gas temperature in the centre increases to about 6000 K, and the conversion and energy efficiency are reduced [1, 3, 4]. It has been suggested that the transition from diffuse to contracted plasma occurs due to thermo-chemical instability, arising from thermally driven endothermic CO_2 dissociation reactions [7], and that the size of the contracted plasma has a radius comparable to the skin-depth [8].

In both regimes the gas temperatures indicate that the thermal dissociation is either present (diffuse mode) or dominant (contracted mode) CO_2 dissociation mechanism. There are two major drawbacks of the thermal dissociation; considering a simple thermal equilibrium of CO_2 gas, *the energy efficiency is limited* to $\sim$ 50% at 3000 K, and $\sim$ 30% at 6000 K [3], and *the conversion is limited* due to the recombination reactions taking place in the effluent:

$$O + CO + M \rightleftharpoons CO_2 + M \qquad\qquad CO + O_2 \rightleftharpoons CO_2 + O \tag{1}$$

It has been suggested that fast cooling, i.e. temperature quenching in the order of 10^7 K/s could minimise the impact of the recombination reactions in the effluent [9, 10, 4]. The fast gas quenching reactions can be ideal quenching, where the conversion achieved inside the resonator is preserved, or super-ideal quenching, where CO_2 conversion is increased by utilisation of O radicals by CO_2 molecule:

$$CO_2 + O \rightarrow CO + O_2 \tag{2}$$

The model of Vermeiren et al. has shown that the gas quenching of warm thermal plasmas at 3000-4000 K can dramatically improve conversion and energy efficiency by quenching at maximum conversion [11]. In the experimental conditions of the plasma torch microwave reactor used in this work, it can be expected that the point of maximum conversion will be in the core of the plasma. For the plasma torch used in this work it has been shown that the plasma (defined as an end of the plasma emitting volume) can protrude beyond the resonator into the effluent for several centimetres, being dependent on the pressure and the power, but showing no dependence on CO_2 flow [3].

The plasma can be quenched by using a nozzle in the effluent. The nozzle configuration mounted in the near effluent (close to the resonator exit) of plasma has been used previously for rapid plasma quenching for the production of ultrafine metal and ceramic powders [12, 13], and nanoparticle formation [14]. In these applications the plasma quenching is achieved by expansion through a nozzle that accelerates the gas to supersonic speed, cooling it very rapidly at rates as high as 10^7 K/s. Computational fluid dynamics (CFD) modelling done by Yang et al. demonstrated two mechanisms leading to the reduction of the thermal energy; I) a compressible gas dynamics effect, where part of the thermal energy converts to directional kinetic energy, and II) formation of a strong eddy after the nozzle, which greatly enhances the relative velocity and heat loss of the fluid to the cooling-tube wall [15]. Sekiguchi et al. used "quenching tube", i.e. water cooled copper tubes with different diameters, and they found that narrower tubes (4 mm in diameter) will yield higher CO_2 conversion than larger tubes due to higher heat transfer rates [16]. Li et al. demonstrated improvement of the CO_2 conversion of an arc thermal source, achieving conversion of up to 50 % and energy efficiency of up to 20 % [17]. Bongers et al. compared the nozzle and no-nozzle data of a 915 MHz microwave plasma source at 200 mbar. Using 2.45 Ghz plasma source, the performance of the system was compared without nozzle and with various quenching methods [18].

In this paper we present results for which nozzle of varying diameter are used at two different positions in the effluent, in order to systematically investigate the extent to which a gas constriction in the form of a nozzle can be used to maximise the conversion and energy efficiency of CO_2 dissociation in the microwave plasma. The aim of the nozzle is twofold: I) to force mixing of a swirling gas with the hot plasma gas (3000-6000 K) and induce either ideal quenching, or both ideal- and super-ideal- quenching, and II) to reduce the gas pressure in the effluent to avoid recombination losses. The experimental setup with a microwave plasma torch fitted with a nozzle covers the pressure range 100-900 mbar for different powers and CO_2 flows, and a comparison to the standard configuration without the nozzle is provided.

2. Experimental setup

The microwave plasma setup comprises a magnetron generating microwaves at 2.45 GHz, a manual 3-stub tuner and the microwave plasma torch [19, 3]. The plasma torch consists of coaxial resonator with a pin on the bottom side, it contains four gas inlets mounted tangentially generating a swirling gas motion in the clockwise direction, and a cylindrical resonator, as shown in figure 1. The plasma torch system used in this work is a closed system with a heat exchanger and variable pressure controlled by a vacuum pump and a valve [3]. A standard design used in this work consists of a quartz tube of 30 mm outer diameter and 26 mm inner diameter, with a typical length between 12 cm and 30 cm connected to the heat exchanger with an inner diameter of 38 mm. The measurement with a nozzle in the effluent will be benchmarked against the standard design without the nozzle as described above. The origin of the axial coordinate z is defined as the bottom of the cylindrical resonator. The cylindrical resonator height is 43 mm, above which the plasma is outside the EM cavity. The flow outside the resonator is considered the effluent. Pressure measurements are taken at two positions, inside the resonator (through a hole in the pin of the coaxial resonator), and in the effluent after the heat exchanger.

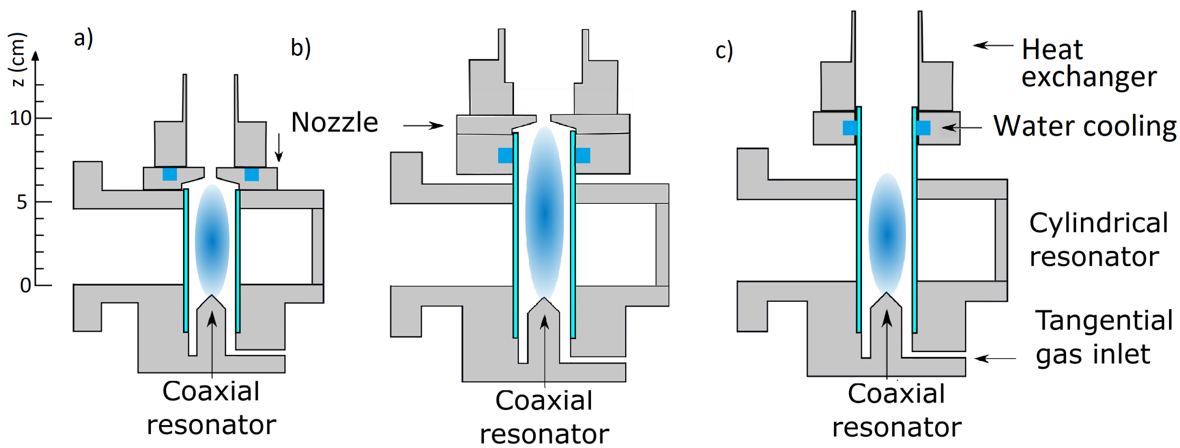

Figure 1. Schematic of the experimental setup showing the plasma torch (comprising a coaxial and a cylindrical resonator), and the nozzle mounted either on a) the resonator (z = 65 mm), or b) on top of the quartz tube (z = 100 mm). Sub-figure c) shows a standard design without the nozzle.

The nozzles are designed as single round constrictions with diameter of 2.5 mm, 5 mm or 10 mm mounted in the effluent The length of the nozzles is 8 mm. The nozzles were mounted either on top of the resonator, at z = 65 mm (Figure 1 a)), or on top of the 12 cm long quartz tube at z = 100 mm (Figure 1 b)). In the latter configuration the nozzle can be positioned at an arbitrary distance from the resonator, defined by the length of the quartz tube. In addition to forcing the gas mixing, the nozzle acts as a heat sink, being directly cooled when mounted on the resonator (Figure 1 a)), and indirectly cooled when mounted on top of the quartz tube (Figure 1 b)). The nozzle in Figure 1 a) is directly cooled by a water (kept at 20° C) running through it, and the nozzle in Figure 1 b) is in direct contact with the component that has the water (kept at 20° C) running through it. The blue rectangles in Figure 1 show the position of water cooling. In either case, no change on any of the nozzles has been observed after the measurement, no melting or erosion of the nozzles made of copper, nor any carbon deposition. The heat exchanger is mounted directly after the nozzle in both cases.

The transition between the diffuse and the contracted plasma modes occurs between 100 mbar and 200 mbar, depending on the power and the CO_2 flow. Figure 2 illustrates the relative size of the nozzles with diameters of 2.5 mm, 5 mm or 10 mm with respect to the contracted plasma diameter (without the nozzle) at a pressure of 900 mbar, a CO_2 flow of 10 slm, and power of 2400 W. The figure 2 is intended to give an idea of relation between the plasma size and the nozzle, and we have no indication if the plasma size changes when the nozzle is mounted. The plasma appears to be slightly off centre due to imperfect alignment of the mirror reflecting the axially integrated light from the plasma towards the ICCD camera. The details of the ICCD plasma imaging can be found elsewhere [3]. The diameter of the plasma without the nozzle becomes wider with increasing power, expanding from 4 mm at 900 W to about 8 mm at 2700 W [3]. Hence, a nozzle diameter of 2.5 mm is expected to be smaller than the diameter of the plasma, independent of input power.

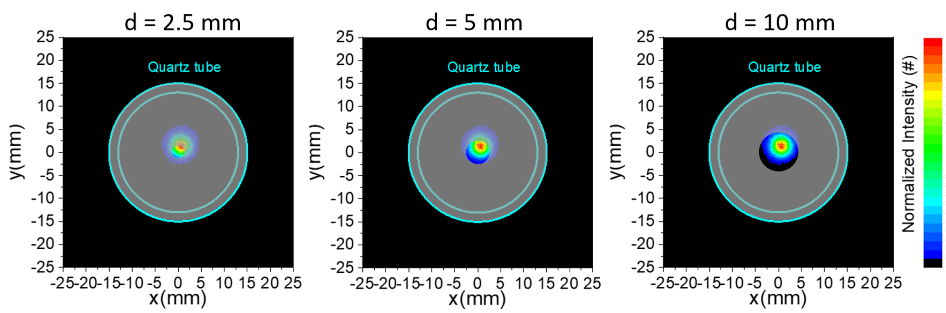

Figure 2. The grey overlay with a hole in the middle represents the size of the nozzle with respect to the size of the contracted plasma emission at 900 mbar, with the respective nozzle diameter inscribed on top of the figure. The image shows the plasma being slightly off centre.

The mass spectrometer is used for sampling the gas in the effluent downstream of the heat exchanger, to determine the relative molar flows of the non-reactive molecules (CO_2, O_2, CO; and N_2 for leak monitoring). The comprehensive description of our mass spectrometry setup and the error analysis can be found in our recent paper [20]. Possible leakage of air was excluded since in our measurements we also measured the atomic nitrogen at mass 14 to detect any possible leaks. From the determined flows the conversion χ_{CO_2} and the energy efficiency η of the CO_2 conversion process are calculated. The conversion is calculated using the following equation [20].

$$\chi_{CO_2} = \frac{2 - 2\frac{\dot{n}_{CO_2,out}}{\dot{n}_{total,out}}}{2 + \frac{\dot{n}_{CO_2,out}}{\dot{n}_{total,out}}} \tag{3}$$

where $\dot{n}_{CO_2,out}$ and $\dot{n}_{total,out}$ are molar flows of CO_2 only, and sum of CO_2, CO, and O_2, respectively. For the calculation of the energy efficiency η the specific energy input (SEI) is needed:

$$SEI = \frac{0.0138\ power[W]}{flow[slm]} \tag{4}$$

$$\eta = \frac{\chi_{CO_2}\Delta H}{SEI[eV/molecule]} = \frac{\chi_{CO_2} flow[slm]\ \Delta H}{0.0138\ power[W]} \tag{5}$$

with ΔH being the standard enthalpy of the dissociation reaction of the CO_2 molecule of 2.93 eV/molecule.

In this paper 900 mbar is used to represent atmospheric pressure conditions. In the laboratory the standard pressure is about 950 mbar. The vacuum tightness of the setup is achieved by use of rubber O rings. Due to the high temperatures of the gases, it is possible that some of the O rings will loose integrity and the vacuum tightness will be lost. In order to avoid leak of dangerous gases, e.g. CO, in the lab, a slight under-pressure is maintained inside the system therefore pressures between 900 and 950 mbar are used. Several times the performance of our plasma system was tested in the pressure range 850-1000 mbar, and the difference of the results was always much smaller compared to the systematic error bars.

3. Results and Discussion

Throughout this section the results obtained with the nozzle at z = 65 mm are shown in blue colour, the results obtained with the nozzle z = 100 mm are shown in red colour, and the results in the standard setup without nozzle are shown in black colour in figures.

3.1. Pressure scan

Figure 3 shows the conversion as a function of the pressure (measured in the resonator) at a fixed CO_2 flow of 10 slm, and a power of 1500 W. Figure 3 a) shows the results for the nozzle mounted at z = 100 mm, and figure 3 b) shows the results for the nozzle mounted at z = 65 mm. For both configurations, the largest improvement of the conversion compared to the standard configuration is found at high pressures, whereas at lower pressures, such as 200 mbar, the conversion is identical or lower compared to the standard configuration. Between 100 mbar and 200 mbar the plasma appearance changes from diffuse plasma at lower pressures, towards contracted plasma at higher pressures [3, 7]. This transition in figure 3 is marked with the vertical dashed line.

The pressure was measured both in the resonator, and in the effluent. For all measurements with the nozzle of 10 mm diameter, no difference in pressures was observed. For the nozzle with 5 mm diameter, at lower pressure some difference of up to 40 mbar between the effluent and the resonator has been measured, being lower in the effluent. At higher pressure the pressure difference for 5 mm nozzle was negligible. The pressure is regulated by the valve in front of the vacuum pump, and when the valve opening is small (high pressure), the nozzle diameter of 5 mm is large in comparison, and pressure difference between the resonator and the effluent is negligible. When the valve opening is large (low pressure), the nozzle diameter of 5 mm acts as a bottleneck, resulting in the observed pressure difference. For the nozzle with 2.5 mm diameter, a significant pressure difference was observed for all pressures, and more details are given in section 3.5.

The results demonstrate that the pressure dependence of the conversion is

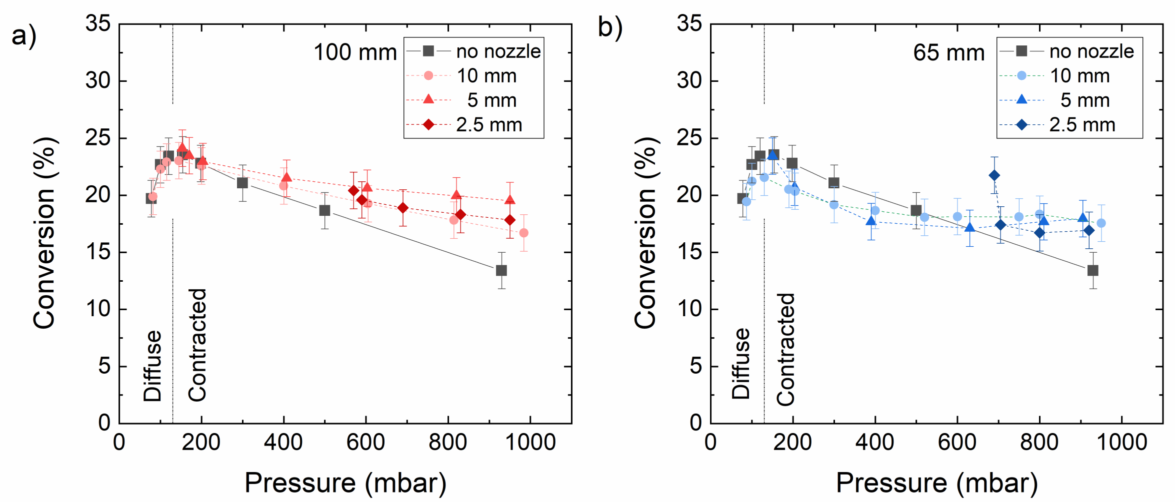

Figure 3. Conversion of the microwave CO_2 plasma as a function of the pressure (measured in the resonator) with a) nozzle at position z = 100 mm, and b) nozzle at position z = 65 mm. The black line stands for conversion without the nozzle, and coloured darker symbols are for smaller nozzle diameter. CO_2 flow was 10 slm and power was 1500 W (SEI = 2.07 eV/molecule).

influenced by the position of the nozzle. Looking over the complete pressure range, the position of the nozzle at z = 100 mm yields slightly better improvement of the conversion compared to the results with the nozzle mounted at z = 65 mm. For the nozzle at z = 100 mm, the conversion improvement is observed for all pressures above 300 mbar, and the highest improvement is for the nozzle with a diameter of 5 mm. For the nozzle at z = 65 mm, the conversion improvement is observed only for pressures above 600 mbar. We can speculate that vicinity of the nozzle to the resonator could induce a perturbation of the flow pattern inside the resonator due to the constriction, or the metal nozzle could perturb the microwave power deposition limiting the active region. Optical emission spectroscopy measurement in the effluent show absence of plasma emission associated with the CO_2 plasma(such as C_2 bands and O atomic lines), indicating that the plasma is confined to the volume below the resonator.

These trends can be better understood when considering the relationship between the length of the plasma and the nozzle position. The nozzle should force mixing of the hot plasma gas and the surrounding colder gas, thus cooling the plasma gas, and as a result reduce the recombination reactions in the effluent. If the nozzle is placed too far from the end of the plasma, the recombination reactions might already take place, and the nozzle induced gas mixing might be dimished. For example, without the nozzle, in the power range 600 W - 2700 W the length of the plasma increases with the power from 35 mm-55 mm (at 200 mbar), from 50 mm-80 mm (at 500 mbar), and from 50 mm-100 mm (at 900 mbar)[3]. Therefore, at 200 mbar the nozzle at both positions is placed after the plasma, and might be too far away to produce any effect.

3.2. 200 mbar - power dependence

The lack of improvement at 200 mbar is independent of the power, figure 4 shows the conversion and the energy efficiency of the measurement with varying power at fixed CO_2 flow of 10 slm, and pressure of 200 mbar. Only the measurements with the nozzles with diameters of 5 mm and 10 mm are shown, as with the 2.5 mm nozzle it was not possible to achieve the pressure of 200 mbar with the CO_2 flow of 10 slm. More details on the plasma torch performance at low pressure conditions with the 2.5 mm nozzle are given in section 3.5.

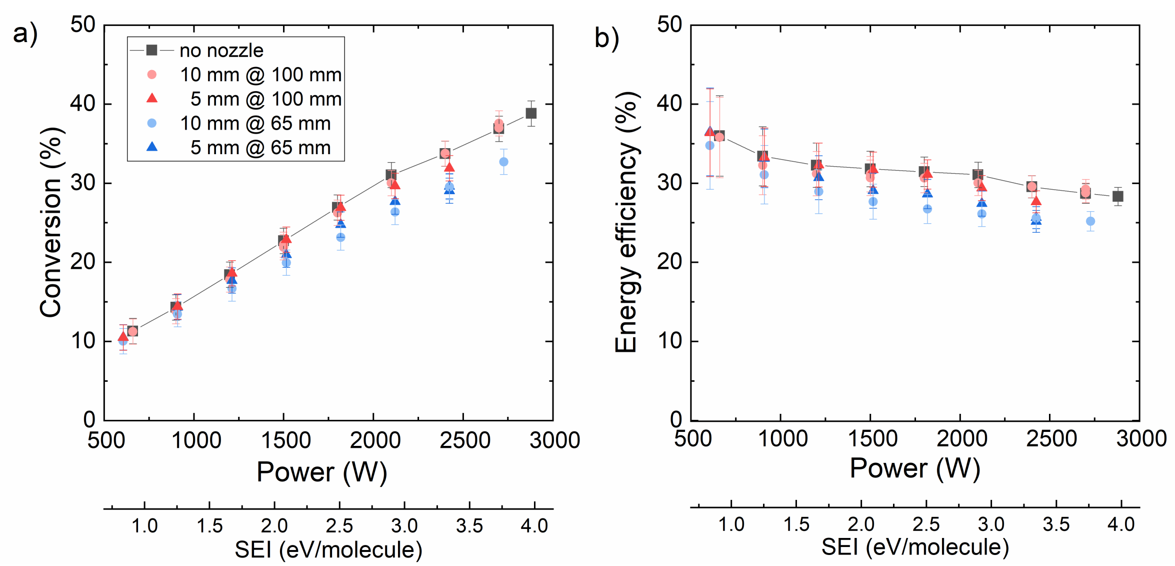

Figure 4. a) conversion and b) energy efficiency of the microwave CO_2 plasma as a function of power. The black line represnts the conversion without a nozzle, and coloured symbols are conversion with nozzles. The pressure was 200 mbar and CO_2 flow was 10 slm.

The results demonstrate a similar trend for all power levels, indicating that the use of the nozzles at 200 mbar results only in comparable or lower values for conversion and energy efficiency compared to the standard configuration.

3.3. 900 mbar - power dependence

Figure 3 showed that the largest improvement of the conversion occurs when the nozzle is used at atmospheric pressure. In figure 5 the conversion and the energy efficiency as a function of power at fixed CO_2 flow of 10 slm, and pressure of 900 mbar are shown. Unlike at 200 mbar, the power scan at 900 mbar shown in figure 5 demonstrates that the different nozzle diameters and positions yield different dependences on the power.

Roughly two trends of the conversion increase compared to the standard configuration can be observed in figure 5. For the nozzle mounted at z = 65 mm the conversion rate is improved already at low power, remaining high as the power increases (except for the 10 mm nozzle above 1500 W). For the nozzle mounted at

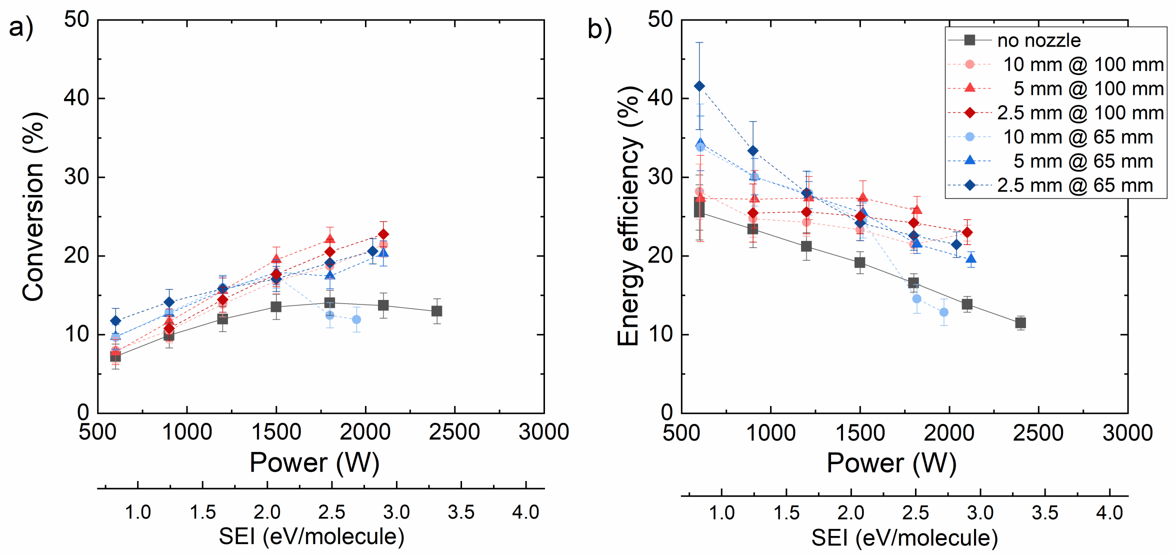

Figure 5. a) conversion and b) energy efficiency of the microwave CO_2 plasma as a function of power. The black line stands for conversion without the nozzle, and coloured darker symbols are for smaller nozzle diameter. Pressure is 900 mbar and CO_2 flow is 10 slm.

z = 100 mm, there is no improvement at the low power, but the improvement in the conversion increases with the higher power. At low power (low SEI) it can be observed that even relatively small improvement in the conversion when using the nozzle leads to a strong improvement in the energy efficiency. For example, for a nozzle mounted at z=65 mm with 2.5 mm diameter, conversion increases from 7% to 12%, yet the energy efficiency increases from 25% to 41%.

As mentioned earlier the length of the plasma at 900 mbar without the nozzle increases with the power from about 50 mm at 500 W, towards 100 mm at 2700 W [3]. For the nozzle mounted at z = 100 mm, at low powers the end of the plasma is below the nozzle, therefore the nozzle might be placed too far away from the plasma to yield any effect. With increasing power, the plasma elongates and the effect of the nozzle at z = 100 mm results in the increased conversion. One of the effects of the improved conversion with a nozzle at z = 100 mm is that the energy efficiency does not exhibit a reduction with increasing power, but rather it remains at a level of about 25 %.

3.4. 900 mbar - flow dependence

Figure 6 shows the influence of the nozzle on the conversion and energy efficiency for CO_2 flows in the range 5-40 slm, at fixed power of 1500 W and pressure of 900 mbar. For the nozzle with 2.5 mm diameter a CO_2 flow of 40 slm resulted in pressures above 1000 mbar so no measurements could be done. The largest improvement of the conversion is observed for low flows, and for the smallest nozzle diameter of 2.5 mm.

The conversion measured in the standard configuration without the nozzle increases with specific energy input (SEI) (i.e. decreases with the flow) up to 2 eV/molecule

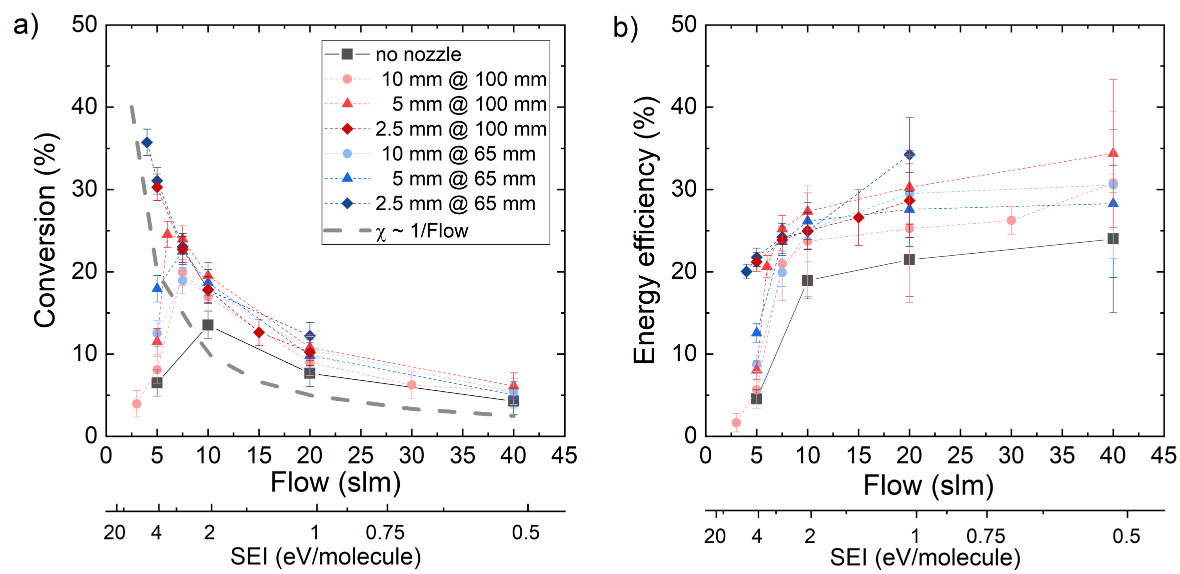

Figure 6. a) conversion and b) energy efficiency of the microwave CO_2 plasma as a function of CO_2 flow. The black line stands for conversion without the nozzle, and coloured darker symbols are for smaller nozzle diameter. Pressure is 900 mbar and power is 1500 W.

after which it exhibits a decrease. The relation between the conversion and the flow is inversely proportional, which is marked with grey dashed line in figure 6 a). This observation is consistent with low CO retention obtained at low flows by Wolf et al. [4]. They have compared the energy efficiency with respect to the post-discharge CO retention. They have used the post-discharge CO retention as a useful measure of CO remaining in the cooling trajectory of dissociation products and defined as ratio of CO molar flow at the measurement position and maximal expected CO molar flow obtained from the model. They showed that the lowest energy efficiency is obtained for low flows where the post-discharge CO retention was lowest.

The reason for low conversion at low flows in standard configuration (lower than 10 slm) can be explained by lack of efficient gas mixing after the plasma. The efficiency of such mixing (intrinsically determined by the temperature gradients), the temperature, and the pressure determine the fraction of CO that is preserved. The probable mechanism that is contributing to this effect is the cooling capacity of the cold gas. A fluid dynamic model of a CO_2 microwave discharge in standard configuration indicates that at the end of the plasma a mixing between the hot plasma and the surrounding CO_2 gas can occur, being responsible for the quenching of hot plasma gas [21]. Furthermore, at 900 mbar D'Isa et al. showed that the total amount of CO produced in the discharge was in the range 0.5-3 slm, and it showed weak dependence on the CO_2 flow in the range 10-100 slm [3]. Thus, the fraction of CO_2 which does not contribute to the plasma is smaller the lower the flow, eventually leading to an insufficient cooling capacity at high SEI.

The positive effect is evident as shown in Figure 6 and can be observed for every flow studied. It is expected that the nozzle enhances the cooling of the plasma effluent, by enforcing the mixing of all the gas injected, improving utilisation of the cooling power of the CO_2 gas injected and dissipating part of the thermal energy into the nozzle components. Consequently, an improved cooling of the hot plasma would lead to a reduced recombination and maximisation of the post-discharge CO retention. The expectation arises from the previous measurements, where the cooling rates measured in pulsed conditions indicated a cooling rates in the order of 10^6 K/s (with trend to increase at lower pressure) [21]. These observed cooling rates are driven only by the temperature and pressure gradients, and are insufficient to achieve the ideal quenching (according to the literature, cooling rates of 10^7 K/s are required [9]). Therefore, by enforcing the gas mixing in the nozzle a larger cooling rates are expected. The cooling capacity of the cold gas can however be limited, which can be observed at Figure 6 b) which shows that despite the effect of the nozzle the energy efficiency at 5 slm is lower than the one observed at higher flows. The most efficient configuration in terms of the improved conversion is the 2.5 mm nozzle, where the highest conversion can be observed also at 5 slm, the reason can be both a better gas mixing or a better energy exchange between the gas and the nozzle components. The conversion with the 2.5 mm nozzle in Figure 6 a) exhibits a trend that is similar to the inverse correlation between conversion and flow (marked as grey dashed line in figure 6 a)).

3.5. Indication of supersonic expansion

As mentioned earlier, in addition to cooling of the hot plasma gas with surrounding colder gas, second mechanism can be expected; compressible gas dynamics effect, where part of the thermal energy converts to directional kinetic energy. The supersonic conditions could only be met while using the nozzle with 2.5 mm diameter, which limits the minimum pressure in the resonator for which the measurements can be done. Figure 7 a) shows the comparison of conversion between the standard configuration and the configuration with the 2.5 mm nozzle, for CO_2 flows of 5 slm and 10 slm, as a function of pressure inside the resonator. Figure 7 b) shows the same data plotted as a function of the pressure in the effluent. For the lowest pressures achievable for a 2.5 mm nozzle, the relative pressure difference between the resonator and the effluent is larger than 2, indicating that the gas expanding in the effluent is achieving supersonic velocity with Mach number M>1. The highest achieved M was about 2, as marked on Figure 7 a) for nozzle at z = 65 mm for both 5 slm and 10 slm.

The Mach number was calculated assuming isentropic flow relations [22]:

$$M = \sqrt{\frac{2}{\gamma - 1}\left(\left(\frac{p_{effluent}}{p_{resonator}}\right)^{\frac{1-\gamma}{\gamma}} - 1\right)} \quad (6)$$

with $p_{effluent}$ and $p_{resonator}$ being the pressure measured in the effluent and in the resonator, respectively, and γ the ratio of specific heat. The exact value of the Mach number should be taken with reserve, as the gas in the microwave plasma torch is a high enthalpy gas flow for which the assumption of reversibility is doubtful due to the fast quenching and because of heat dissipation into to the nozzle.

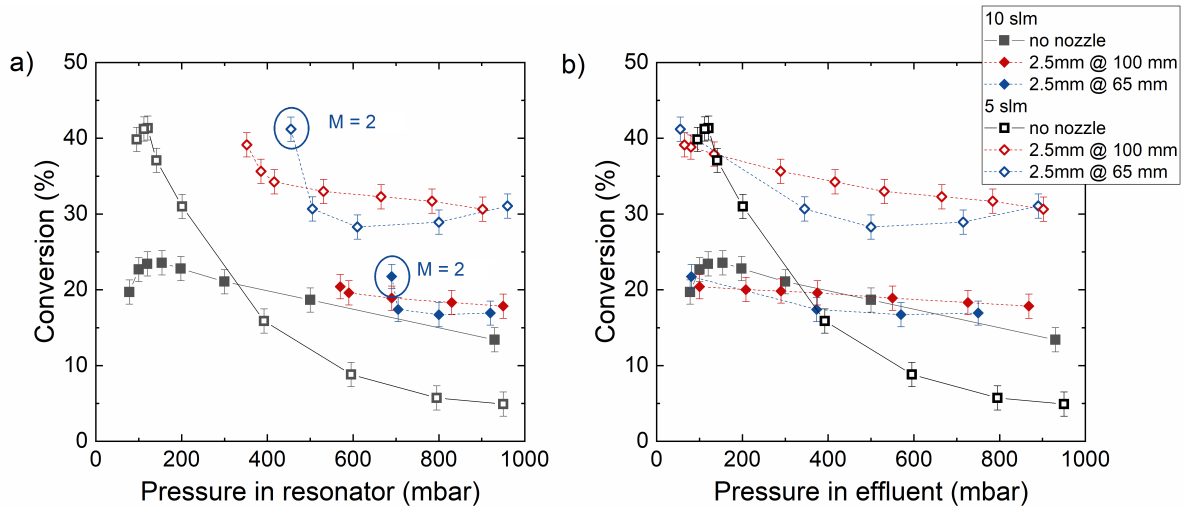

Figure 7. Conversion of the microwave CO_2 a function of a) the pressure in the resonator, and b) the pressure in the effluent. The black line stands for conversion without the nozzle, and coloured symbols are for nozzle diameter of 2.5 mm. The full symbols are for the CO_2 flow of 10 slm, and the empty symbols are for the CO_2 flow of 5 slm. The power is 1500 W (SEI (10slm) = 2.07 eV/molecule, SEI (5slm) = 4.14 eV/molecule).

Figure 7 demonstrates that, when lowering the pressure, the conversion increases, which could be I) reduction of the recombination rates due to lowering of the pressure and II) temperature reduction due to the effect of supersonic expansion. We do not have indication of other possible mechanism, which could lead to an improved conversion such as change in the plasma volume, or change in the temperature of the plasma. Our setup limits us in observing the length (height) of the plasma as it is obstructed by either the resonator (65 mm case) or by cooled O rings below the nozzle (100 mm case) as can be seen in Figure 1. However no significant change in the plasma width has been noticed. The measurements of rotational and vibrational temperature of C_2 emission with a nozzle were done and the results are comparable to the values reported in the setup without the nozzle [3].

I) Figure 7 b) demonstrates that comparing the conversion values of the standard configuration with the conversion with a 2.5 mm nozzle taking into account the pressure in the effluent, the results at higher pressure now become comparable with the conversion at low pressure obtained in the standard configuration without the nozzle, and also comparable to the other nozzle configurations (shown in figure 3). The recombination in the effluent will be reduced because of the pressure reduction, with the reaction rate depending on the product of the two reactant densities, the reaction rates will exhibit squared reduction with linear reduction of the pressure. From literature results [3, 4, 7, 8, 20] it is well established that reducing the pressure reduces the recombination in the effluent. Thus, a lower pressure in the effluent after the nozzle will contribute to reduction of the recombination. Moreover, figure 7 b) and the fact that the plasma torch conversion is always below the maximum observed conversion at 200 mbar suggests a dominant effect due to the operating pressure. The pressure in the resonator is always above the contraction pressure, which implies a high temperature in the resonator. The pressure in the effluent controls the CO retention in the effluent, which below 200 mbar is close to 1 [4].

II) Increased conversion as a result of reduction of the temperature due to the part of the thermal energy getting converted to a directional kinetic energy. Focusing only on the temperature reduction due to gas expansion in the effluent, one can estimate that for M $\sim$ 2 the ratio of the average temperature in the effluent and the resonator ($T_{effluent}/T_{resonator}$) is about 0.6 under the assumption of isentropic expansion (see above for discussion). Where $T_{effluent}$ and $T_{resonator}$ are gas temperatures of the mixed hot and cold gas in the effluent and in the resonator, respectively. This temperature reduction in the effluent could contribute to the total temperature reduction that is preventing recombination to CO_2 and enhancing CO retention (i.e. reducing the recombination). The maximum effect in case of the supersonic expansion would be enhanced cooling rate that would lead to CO retention close to 1.

Since both mechanisms will manifest itself in the same manner: maximising CO retention, it is hard to conclude which of the mechanisms is dominant. Further investigation is needed to explore the performance of the system at different degrees of supersonic expansion and to understand the magnitude of the temperature drop and identify its contribution.

3.6. Overview of results

As shown in figure 3, for a given flow and power, the largest conversion in a standard configuration without the nozzle will be at pressures in the range of 100-200 mbar, and use of the nozzle at these pressures results in similar or lower conversion. The conversion as a function of power at 200 mbar is plotted using empty symbols in a conversion - energy efficiency graph in figure 8. The power scan at 900 mbar is plotted in the same graph using black square symbols.

The blue symbols in figure 8 are the symbols obtained when using the nozzle at 900 mbar. This figure of merit demonstrates that by using the nozzle it is possible to significantly increase the performance of the plasma torch at atmospheric pressure, both in conversion and energy efficiency towards values achieved at 200 mbar. This finding becomes particularly important when industrial application is considered. Here, and in most of the publications on the plasma conversion only the microwave power delivered to the plasma is considered. However, for the calculation of the total (wall-plug efficiency) one needs to consider the efficiency of the magnetron used for the microwave generation, and the power consumption of all peripheral components required to run the discharge, e.g. vacuum pump, chiller, etc., as pointed out, for example, in [10]. The results presented in Figure 8 demonstrate that relatively high conversion and energy efficiency

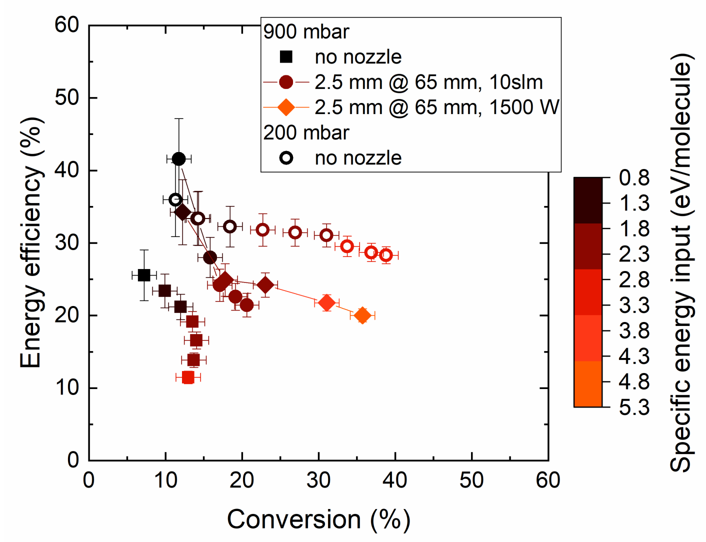

Figure 8. Conversion and energy efficiency of the CO_2 microwave plasma torch. At 900 mbar, square symbols stand for results obtained in a standard configuration without the nozzle, and circular and rhomboid symbols stand for results obtained with the nozzle at fixed parameter of either 10 slm or 1500 W. At 200 mbar, hollow symbols stand for results obtained in a standard configuration without the nozzle. The colour coding of the symbols is according to SEI, with the colour scale of SEI given on the right side.

can be achieved without using the vacuum pump, which would lead towards an improved wall-plug efficiency.

4. Conclusion

In this work we present a detailed investigation of the CO_2 conversion and the energy efficiency in a microwave plasma torch fitted with a nozzle mounted in the effluent, in the pressure range 100-900 mbar. The idea behind employing the nozzle in the effluent is that the nozzle should force mixing of the hot plasma gas and the surrounding colder gas, thus reducing the recombination reactions in the effluent by inducing ideal quenching or reducing the gas pressure in the effluent to avoid recombination losses.

At low pressures, 200 mbar and lower, no effect was observed (except a reduction in efficiency for the nozzle mounted at 65 mm), probably due to the length of the plasma at 200 mbar being shorter than 55 mm [3], and the nozzles placed at z = 65 mm z = 100 mm appear to be placed too far from the plasma to yield any effect. At pressures above 200 mbar, improvement in conversion was observed, being strongest at 900 mbar. The nozzle is particularly efficient for low CO_2 flows (below 10 slm) corresponding to SEI above 2 eV/molecule at pressure of 900 mbar. For example, at 5 slm, 1500 W and 900 mbar, without the nozzle the conversion is about 5%, and with the nozzle it increases to 35 % for a nozzle with 2.5 mm diameter. These results indicate that the position of the nozzle, and the nozzle diameter must be optimised for given plasma size which depends on the applied power and the pressure.

In a standard configuration, the low conversion at low flows can be explained by lack of gas mixing after the plasma, that leads to a strong CO recombination (minimal post-discharge CO retention). The nozzle forces the hot and cold gas to mix, and in that way it is possible that use of the nozzle improves the cooling of the plasma effluent, leading to improved utilisation of the cooling power of the CO_2 gas injected, and dissipating part of the thermal energy into the nozzle components. Consequently, fast cooling of the hot plasma could lead to a reduced recombination and maximisation of the post-discharge CO retention. This effect is most efficient for the smaller nozzle diameter (strongest mixing), and for the lower CO_2 gas flows where the recombination has the largest impact on conversion.

When using 2.5 mm nozzle at sub-atmospheric pressures, a condition with a large difference between the pressures in the resonator and in the effluent are observed, that under isentropic assumption could lead to the supersonic expansion into the effluent with Mach numbers up to 2. The condition of large pressure difference was accompanied by an additional increase in conversion, stemming from one of two possible mechanisms: I) reduction of the recombination rates due to lowering of the pressure in the effluent and II) temperature reduction due to the possible effect of supersonic expansion. Although a contribution of the latter cannot be excluded a priori, the observed performance can be entirely explained considering the effect of the pressure both in the resonator and in the effluent.

The figure of merit demonstrates that by using the nozzle it is possible to significantly increase the performance of the plasmas torch at 900 mbar, both in conversion and energy efficiency towards values achieved at 200 mbar, which is an important step towards industrial applicability of this technology, and potentially improved wall-plug efficiency.

5. References

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