Elucidating the role of gas dynamics in the vortex-confined microwave plasma on CO_2 dissociation efficiency

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Abstract: The role of gas dynamics and its interplay with a microwave sustained vortex stabilized plasma is investigated. Based on CFD modelling and experimental values of the reactor efficiency, it is found that the vortex flow generates a recirculation cell that effectively isolates the plasma with a diffusion limited transport boundary towards the exhaust. The efficiency limitations of CO_2 conversion in the reactor are successfully captured using a 2-temperature closed reactor model based on thermodynamic equilibrium conditions.

Keywords: solar fuels, CO_2 conversion, microwave plasma, vortex confined plasma, gas dynamics

1. Introduction

In face of the energy transition, CO_2 forms an attractive feedstock for both production of energy-dense solar fuels and as source of carbon for value-added chemicals. CO_2 microwave plasmas have been studied extensively in context of CO_2 conversion due to a favourable combination of high efficiency and power scaling potential over other technologies. A vortex-flow is commonly utilized in such high-power RF discharges, and more generally in high-intensity combustion chambers, to provide insulation and stabilization [1]. The attractive properties of the vortex flow are attributed to the formation of toroidal recirculation zones. Several reports can be found on plasma-driven dissociation of molecules in this type of flow configuration, with the aim of maximizing efficiency. In the case of CO_2 record efficiencies of 80% are reported, accredited to vibrational dissociation, at optimized values of reduced field, gas temperature and values of pressure and specific energy input (SEI) [2]. More recent research shows similar qualitative discharge behaviour for given pressure and specific energy input, however the core temperature of over 3000-5000 K typically observed in such discharges and the efficiency limit of 40-50% suggests that thermal dissociation is the dominant dissociation mechanism [3][4]. This apparent division in results found in the literature in terms of energy efficiency is still not fully understood.

Although focus is often laid on characterization of the discharge conditions in the plasma core in attempts to understand the reactor efficiency values, the role of the gas dynamics is often ignored. In this contribution, we report on the effect of gas dynamics in the forward-vortex-confined discharge, and show how it governs the efficiency of CO production. Based on a closed-system 2-temperature reactor model, under assumption of chemical equilibration followed by an ideal quenching trajectory, the efficiency behaviour of the plasma can be essentially captured. It is shown that the flow dynamics have little influence on the plasma core conditions, while the extraction of products is limited by diffusion due to the vortex flow dynamics in the vortex-stabilized microwave plasma. In light of this finding, the interpretation of specific energy input (SEI) as a plasma parameter is revised.

2. Flow dynamics of the forward-vortex configuration

A tangential flow component in a cylindrical flow geometry can profoundly change the flow characteristics compared to its laminar Poiseuille flow counterpart. This can be illustrated by considering that the tangential flow (or swirl) leads to a pressure gradient directed radially outwards. This effect reduces along the axis away from the injection plane as the swirling intensity decays. Provided the vortex flow is sufficiently strong, a positive pressure gradient on-axis will form which leads to local flow reversal [1]. Using CFD modelling, a flow pattern for the forward vortex flow configuration is visualized in the reactor cross-section in Fig. 1.

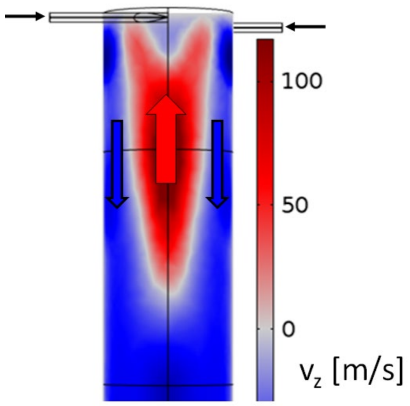

Fig. 1: Forward vortex flow - On-plane projection of the z-component of the gas flow

This characteristic flow structure in the toroidal plane is visualized by projection along the cylindrical axis, with the flow reversal zone clearly visualized in red. The simulations also unveil the more subtle property of recirculation zone in the fact that the flow lines that pass through the recirculation cell are closed by closing in on themselves. The open flow lines on the other hand originate from the injection point and flow in a helical manner along a layer close to the wall toward the exhaust. Since no flow lines go directly from the plasma region to the exhaust, adjective transport is effectively blocked as a means of product extraction from the plasma region. Reaction product extraction from the forward-vortex flow reactor is diffusion limited.

3. Two-temperature reactor model

In order to link the plasma parameters to the reactor performance in terms of energy efficiency of CO production, a simplified reactor model is employed based on a two-temperature description. The reactor is represented as a closed system gas volume characterized by the recirculation cell temperature T_1 and pressure p, which is maintained under equilibrium composition conditions. Heating of the CO_2 to T_1 shifts the chemical equilibrium towards the dissociation products. The reaction products in the recirculation cell that move towards the peripheral region of the CO_2 gas blanket undergo rapid cooling to a temperature of the reactor wall T_0. In this way dissociation products are stabilized from the reverse reactions. The maximal efficiency of this quasi-equilibrium process is achieved under ideal quenching conditions, i.e. the conversion degree achieved in the heating phase is conserved throughout the cooling trajectory [5], if a cooling rate of 10^6 K/s or greater is realized [3]. The assumptions made in this model are warranted under the following considerations: Based on pulsed tracer experiments, particle residence times in the recirculation cell of approximately 40 ms are found (work in preparation), which is well above the equilibration reaction timescale at the typical gas temperatures in the reactor [3]. Secondly, the closed flow-lines in the recirculation cell and the flow-imposed diffusion boundary leads to a temperature build-up in the core and a strong temperature- and CO gradient towards the open flow lines.

The efficiency of CO_2 decomposition via the ideal thermal decomposition process is calculated regarding the change in mixture enthalpies. In the context of the reactor process, the CO_2 gas is heated from room temperature to T_1. The equilibrium composition at this temperature and pressure is calculated with the Cantera thermodynamics module [6] and the Grimech 3.0 chemistry set. The molar fractions $\boldsymbol{X}= \{X_{co2}, X_{co}, X_{o2}, X_o, X_c\}$ and mixture enthalpy are obtained in this manner as function of gas temperature T and pressure p. During the heating trajectory, the gas composition moves from pure CO_2 to a fully converted mixture of CO and O between 2000 K and 4000 K. Above 6000 K, CO decomposition to C and O becomes significant. The degree of CO_2 conversion α is defined using the equilibrium molar fractions as

$$\alpha = \frac{X_{co}}{X_{co} + X_{co2} + X_c} \tag{1}$$

which is a function of both temperature and pressure. After cooling a certain fraction of the energy invested in the heating process is retained in the form of chemical bonds. The efficiency of the heating and quenching process is related to the mixture enthalpies using

$$\eta_{IQ} = \frac{\Delta H_{mix}(\boldsymbol{X}_{IQ}, T_{300K})}{\Delta H_{mix}(\boldsymbol{X}_1, T_1)} \tag{2}$$

where $\Delta H_{mix}(X, T)$ is the enthalpy change at constant pressure of the gas mixture with composition **X** with respect to pure CO_2 at 300 K. $\boldsymbol{X_1}$ and $\boldsymbol{X_{IQ}}$ are the equilibrium composition in the recirculation cell and the composition after ideal quenching of the mixture respectively. $\boldsymbol{X_{IQ}}$ is obtained by ensuring conservation of conversion degree under stoichiometric conditions - atomic oxygen present in the mixture is assumed to recombine to molecular oxygen, while any carbon recombines with oxygen to form CO_2. A T_0 of 300 K is assumed since the wall temperature is relatively close to the room temperature.

The resulting values as function of temperature for a pressure of 100 mbar are presented in Fig. 2. The ideal quenching efficiency reaches a maximum value of 52% at an upper temperature of approximately 3000 K. Below this value, the conversion at the starting point is insufficient, while at higher temperatures the additional energy investment does not further increase the conversion.

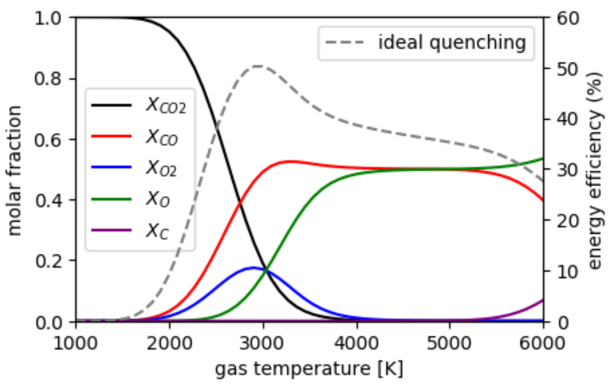

Fig. 2: Thermodynamic equilibrium calculation of the molar fractions and ideal quenching efficiency of CO_2 at a fixed pressure of 100 mbar, as function of temperature.

4. Results and discussion

The CO_2 dissociation is studied in a forward vortex-confined microwave reactor at a power of 1000W and a pressure varying from 50 mbar to 1000 mbar. Details about the reactor design and performance are reported in more detail previously [7]. Plasma core temperatures are obtained via a Doppler broadening measurement of the atomic oxygen line at 777 nm and presented in Fig. 3. For a fixed power, the temperature data follow a single curve as function of pressure. The temperature rise coincides with a radial contraction of the plasma in the transition from the diffuse to the contracted discharge regime. The weak dependence of core temperature on the flow rate shows that the plasma core conditions are not influenced significantly by the flow dynamics. This finding is corroborated by observations obtained with electron density and plasma shape measurements (in preparation).

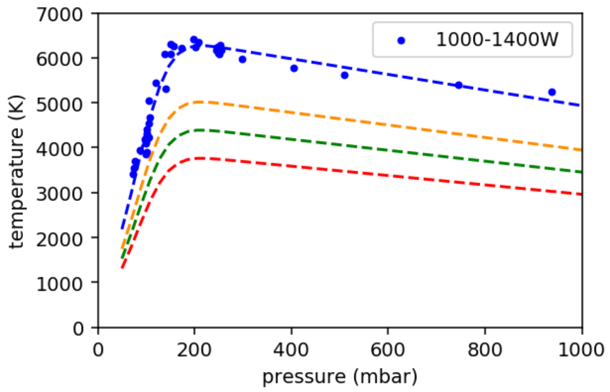

Fig. 3: Core gas temperature measurements as function of pressure. The dashed lines show temperature parameterizations of T_1 in blue (f=1), orange (f=0.8), green (f=0.7) and red (f=0.6).

Since quenching most likely occurs at the periphery of the recirculation-cell rather than in the plasma core, T_1 is most likely substantially lower than the core plasma temperature. Therefore, as a first approximation, the quenching is assessed for different values of T_1 taken as fixed fraction f of the peak temperature measured in the plasma core. The corresponding temperatures curves are indicated in Fig. 3 with the dashed lines. The overall reactor efficiency is experimentally obtained by measuring the conversion in the exhaust using the definition of Eq. 1 with molar ratios obtained with gas chromatography. The efficiency is derived from the conversion by applying $\eta = \alpha \cdot \Delta H_r[eV]/\mathcal{E}_v$, where ΔH_r represents the net CO_2 dissociation reaction enthalpy of 2.91 eV, and $\mathcal{E}_v$ is the global specific energy input of the reactor in eV/molecule.

The experimental results are shown in Fig. 4 together with the ideal quenching efficiency calculation based on Eq. 2. The experimental efficiency curves show a threshold which coincides with a plasma contraction around 100 mbar. At high values of the flow rate (or low SEI) the efficiency plateaus around 35% efficiency. A further rise in pressure leads to an decay of the efficiency, which is strongest for low flow rates. Both the threshold behaviour of the experimental data and plateau of the efficiency obtained at high flow rate is roughly captured by the 2-temperature model. Particularly around f=0.7 the threshold value and the plateau efficiency match well. This value is in line with temperature measurements obtained in the afterglow using rotational Raman scattering in the afterglow surrounding the plasma [8].

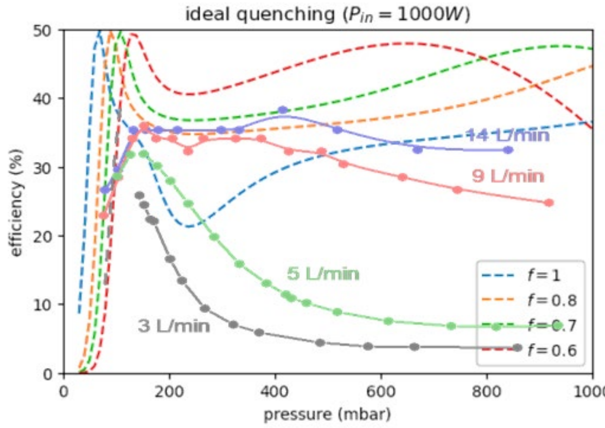

Fig. 4: Experimental efficiency values as function of pressure (dots) and the efficiency limitations obtained from the 2-temperature model (dashed lines)

The threshold and plateau behaviour can be explained in light of the ideal quenching behaviour. At low pressure the core temperature is insufficient to provide significant conversion of CO_2 in the core region. At high pressure the core temperature plateaus at 5000 K to 6000 K, resulting in a corresponding plateau in efficiency. The clear correlation between core temperature and efficiency indicates that the temperature drives dissociation in the plasma region. Interestingly the overall reactor efficiency shows a clear flow-dependence in the plateau region while it is previously established that the plasma core conditions are not influenced significantly. This apparent contradiction can be explained as a consequence of the diffusion-limited behaviour that naturally follows from the vortex-confinement. It is likely that the CO_2 flow around the recirculation cell aids in sustaining both a temperature and concentration gradient at the recirculation cell boundary, both likely contributing to the steepness of the cooling trajectory. As flow rate decreases at fixed power, (thus increasing the SEI), either the concentration gradients or the temperature gradient lowers due to lower thermal mass of the CO_2 flow.

It must be noted that the measured efficiencies are remarkably close to the ideal behaviour predicted using the closed system model. Although the efficiency limit may be underestimated based on the assumptions made in the model, the relatively high efficiency values with respect to the thermodynamic limit may however also be explained by considering super-ideal quenching. The fresh supply of CO_2 in the open system can locally shift the composition towards CO_2, which may promotes the production of CO through the direct endothermic reaction between CO_2 and atomic oxygen. Thermodynamic calculations show that this super-ideal quenching scenario has an efficiency limit of approximately 70% for CO_2 conversion.

5. Conclusions

In this contribution the role of flow dynamics is investigated in vortex-stabilized microwave plasma reactors. While this work focuses on CO_2 dissociation as main application, the conclusions may be extended to other gas species. The flow dynamics have very minor influence on the plasma discharge itself, the influence on the reactor output is nonetheless significant. This notable behaviour is shown to manifest itself as a consequence of the vortex flow in the system, since the formation of central recirculation zone prohibits advective transport from the plasma region to the exhaust. This implies that extraction of CO from the plasma core is limited by diffusion. The separation of the gas dynamic behaviour from the plasma parameters sheds new light on the interpretation of the SEI as a global reactor parameter. Since reactor flow largely flows around the recirculation cell and does not influence the plasma significantly, the SEI should not be regarded as a plasma parameter, but rather a global measure of the production of CO over the efficacy of extraction from the recirculation cell.

The experimental results, and particularly the efficiency of dissociation, are found to agree with the expected diffusion-limited behaviour. A simple closed-system reactor model, assuming ideal quenching, shows that the reactor efficiency is governed by the temperature in the plasma region, which indicates that thermal decomposition in the core is the dominant dissociation mechanism. The flow and pressure dependence indicate that gas flow around the recirculation cell facilitates the quenching process by either sustaining the temperature gradient or concentration gradient. Further research is required to distinguish these two processes and establish the limiting mechanisms. The 2-temperature model can be refined by quantifying the diffusion limitation and capturing the pressure dependence effect using a plug-flow reactor model. Additionally, investigation of the potential role of super-ideal quenching in the reactor may pave the way for further enhancements of the reactor efficiency.

6. Acknowledgement

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7. References

[1] N. Syred and J. M. Beér, Combust. Flame, **23**, 2, (1974).

[2] Y. P. Butylkin *et al.*, Sov. Phys. Tech. Phys., **26**, 5, (1981).

[3] N. den Harder *et al.*, Plasma Process. Polym., **14**, 6, (2017).

[4] D. C. M. van den Bekerom, University of Technology, Eindhoven, (2018).

[5] A. Fridman, Cambridge University Press, (2008).

[6] D. G. Goodwin *et al.*, (2017). [Online]. Available: http://www.cantera.org.

[7] W. Bongers *et al.*, Plasma Process. Polym., (2016).

[8] D. van den Bekerom *et al.*, Plasma Sources Sci. Technol., in press, (2018).