Residence times and Raman composition measurements for reactor design

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Abstract:
This study compares flow phenomena in forward vortex and reverse vortex CO_2 microwave plasma reactors. Nitrogen is pulsed into the forward vortex as a tracer for determining residence times. The measured residence times are 20 times longer than what can be expected based on simple plug flow model. Using Raman spectroscopy, maps of species density and temperature are obtained for both the reverse and forward vortex and reveal different transport mechanisms being promoted in both configurations.

Keywords: microwave plasma, CO_2 dissociation, forward vortex, reverse vortex, Raman spectroscopy, residence time, recirculation

1. Introduction

Multiple research groups around the world [1,2] are currently investigating microwave plasmas for dissociating CO_2 into CO and O_2, where CO can be used a precursor for carbon containing materials or fuels. A common reactor configuration for CO_2 dissociation microwave plasmas is the (forward) vortex configuration (see Fig. 1b). The vortex is created by azimuthally injecting CO_2 gas into the reactor from two sides and promotes axial symmetry inside a reactor's quartz tube. This centres the plasma while cold fresh air flows along the sides of the quartz tube cooling it down allowing for continuous operation. In the forward vortex configuration, the microwave applicator is placed between the inlet and exhaust of the reactor.

A possible consequence of vortex flow is a reduced or even a reversed flow in the centre of the reactor tube [3, 4]. This can increase residence times of reactants and give rise to recirculation. Depending on the objective of a study this might be undesired, which is why reverse vortex configurations are gaining interest in microwave plasma research. In the reverse vortex configuration, the injection and exhaust are at the same side of the microwave applicator (see Fig. 1a). This geometry utilizes the reversal of the flowlines in the centre, averting recirculation.

In this work we quantify the average residence time of the forward vortex reactor by using nitrogen as a tracer. We measure spatially resolved maps of composition and temperature of both the forward and reverse vortex reactor using Raman spectroscopy.

2. Method

Residence times in the forward vortex configuration are measured by axially injecting pulses of nitrogen into the reactor tube. Although the nitrogen has negligible optical emission under the plasma conditions of interest, changes in the integrated optical emission from the plasma are shown to be a reliable measure for the amount of nitrogen present in the plasma zone. The emission of the plasma is recorded with an iCCD camera, which is gated after a variable delay after the nitrogen pulse to yield time resolution and to determine the residence time distribution function for the nitrogen tracer.

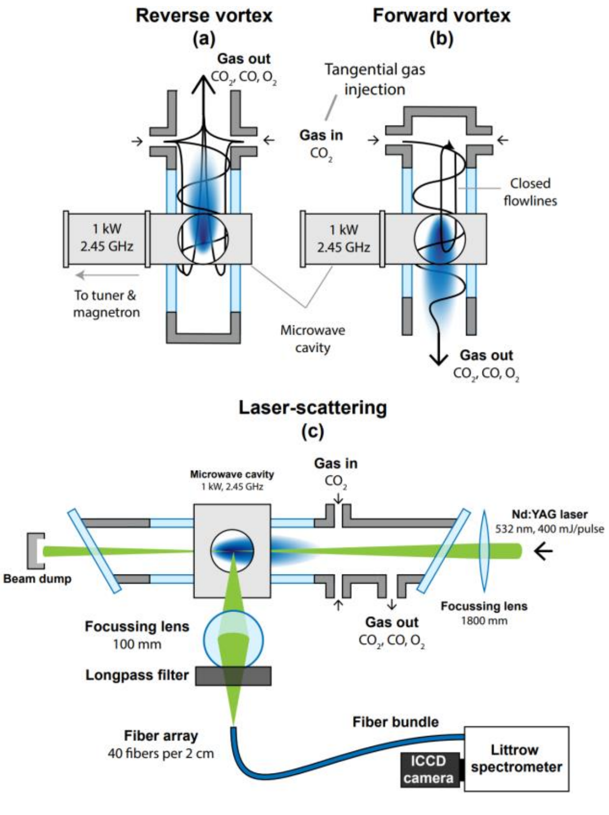

Fig. 1. Schematics of the forward (b) and reverse (a) vortex configurations, with illustrations of flowlines (based on [3]), and a schematic of the laser setup (c) used to assess local densities.

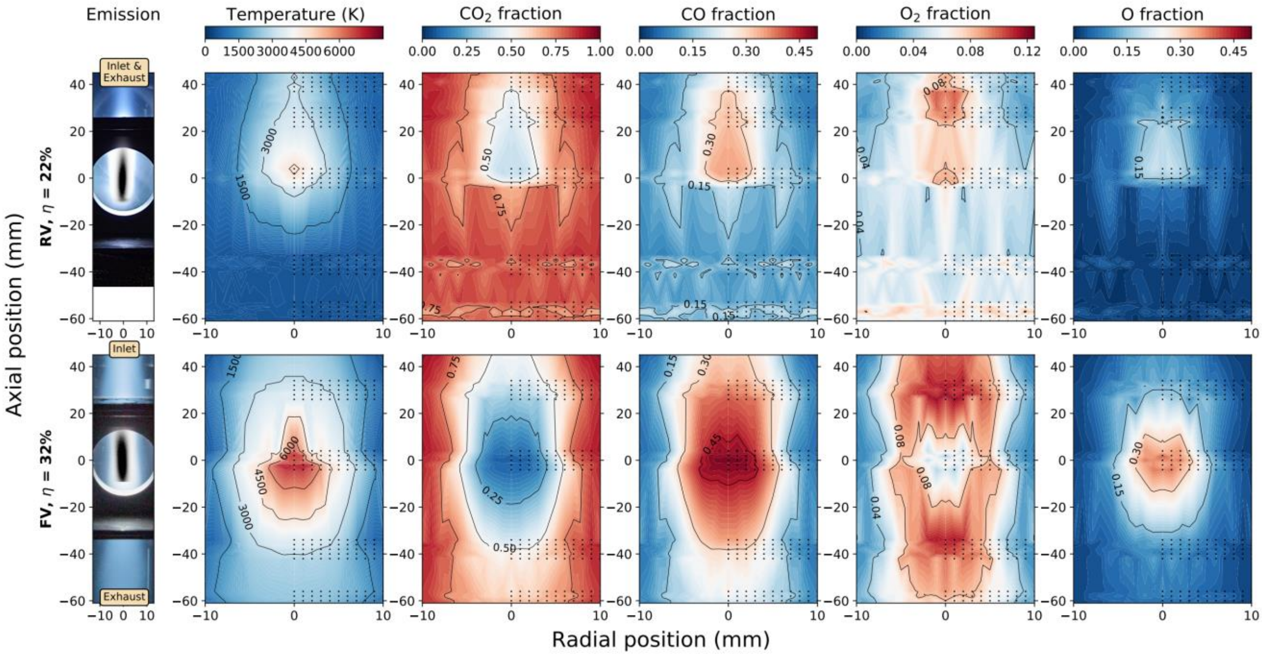

Fig 2: 2D results of rotational Raman scattering in a 120 mbar, 1000 W, 20 slm reverse vortex (top) and forward vortex (bottom, from earlier work [6]). From left to right: Plasma emission (an overlay of total emission and 777 nm oxygen atom emission), rotational temperature, CO2 fraction, CO fraction, O2 fraction and O fraction.

Commonly, plug flow is assumed to estimate the average species residence time. To compare our experimental results with the plug flow assumption, we have determined core gas temperatures from the Doppler broadening of the oxygen 777nm emission [5] and assumed a flat velocity profile along the radius of the tube with that temperature.

For laser Raman scattering measurements, a frequency doubled, vertically polarized Nd:YAG laser (532nm) is focused in the centre of the plasma along the axial direction. Raman scattered light is collected by a fibre array for spectral analysis (see Fig. 1c). Translation the reactor and collection optics yields 2D maps of the composition (CO_2, O_2, CO and O) and temperature. Such maps in forward vortex configuration have been reported before [6]. In this work, the measurements are repeated for 120mbar, 1000W and 20slm in the reverse vortex configuration. These conditions were chosen for their good performance in the forward vortex configuration in terms of energy efficiency.

3. Results and Discussion

Average particle residence times are plotted in Fig. 3 and show 20 times higher values than what can be expected when a plug flow model is assumed. This is a strong indication that flow in the centre of the reactor is reduced or reversed, where the latter implies recirculation.

A signature of reverse or stagnating flow for the forward vortex configuration can be recognized in the composition measurements shown in Fig. 2, where high temperatures and reaction products are found upstream of the plasma. This is in contrast with the reverse vortex measurements (also Fig 2) where the majority of the products appear downstream of the plasma.

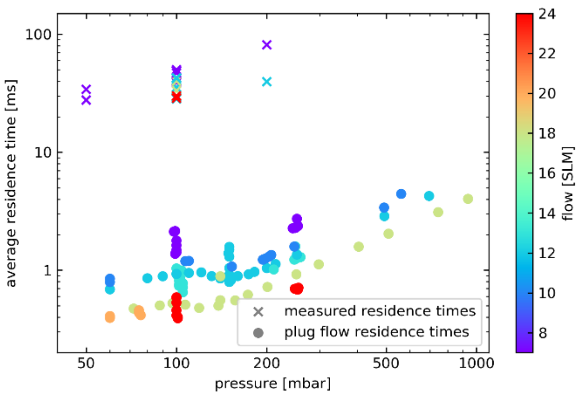

Fig 3: The crosses represent the residence times determined by the pulsed tracer gas. The solid circles indicate calculated plug flow residence times for comparison.

Although both composition measurements are performed under same operating conditions (pressure, total mass flow and power) the temperature difference between reverse and forward vortex are significant. While the forward vortex core temperature exceeds 6000K, the reverse vortex is significantly less hot at 4500K. This is in accordance with higher heat transport due to increased flow velocities through the core of the plasma in the reverse vortex. In the forward vortex configuration, where flow velocities are evidently much lower and possibly recirculation occurs, heat and mass transport rely more on diffusion. We estimate an order of magnitude lower transport rates and accordingly increased plasma residence time. The higher temperatures lead to higher chemical reactions rates and hence explain the higher performance of, in this case, the forward configuration.

4. Conclusion

With the forward vortex relying more on diffusion for effective particle transport in and out of the reactive zone than the reverse vortex, which relies predominantly on direct flow lines for heat and mass transfer, we conclude that the residence time distribution function of the reverse vortex will be more peaked around an average residence time than the forward vortex configuration for the tested operating conditions. Having a more strongly peaked residence time distribution function also allows for a more evenly distributed specific energy input. These considerations are of importance for the engineering of microwave plasma reactors in their scale-up towards industrial reactors.

5. References

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