Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information of "Avoiding solid carbon deposition in plasma-based dry reforming of methane"

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This supplementary information contains details on the gas analysis (section 1), the volumetric production rates (section 2) and the estimation of the plasma dimensions (section 3).

1. Gas chromatography

1.1. Correction factors α and β

Most plasma reactors are plug-flow type reactors where the reactions, taking place in quasi-isobaric conditions, determine a change in the total number of particles, the gas volume and the volumetric flow rate, along the reactor. Particularly in DRM, the change in concentration of the gas mixture components can be significant and the process parameters depending on the volumetric flow rate are affected. Therefore, neglecting the effect of reactions on concentrations and on the gas flux introduces a systematic error in the computation of the process[1]. Furthermore, H_2O is removed prior to injecting the gas in the GC, and some products may be removed from the gas mixture along with H_2O, thus leading to a change in concentration of the remaining components. If not taken into account, these effects can lead to significant errors in conversion, selectivity, etc. To correct for these effects, N_2 is used as an internal standard and added to the gas mixture after the reactor outlet. In this way, two correction factors can be defined:

$$\alpha = \frac{\varphi_{plasma}}{\varphi_{blanc}} = \frac{A_{IS}^{blanc}}{A_{IS}^{plasma}}(1 + \beta) - \beta \qquad \text{(S1)}$$

with φ_{blanc} and φ_{plasma} being the volumetric flow rate before and after the plasma, respectively, and A_{IS}^{blanc} and A_{IS}^{plasma} being the integrated area of the peak detected at the GC of CO_2 or CH_4 with plasma off and on, respectively, and

$$\beta = \frac{\varphi_{IS}}{\varphi_{blanc}}, \qquad \text{(S2)}$$

defined as the flow rate of the internal standard φ_{IS} with respect to the flow rate at the reactor inlet. The factor α corrects for the overall change in flow rate when comparing a blank to a plasma measurement, and can be expressed as a function of β and the peak areas of the internal standard for a blank and plasma measurement. These factors are derived from the work of Pinhão *et al.*[1] by Wanten *et al.*[2]

1.2. Performance parameters

The concentrations for each reactant *i* and product *j*, corrected for the dilution by the addition of an internal standard, can be defined for a blank and plasma measurement as:

$$c_i^{\mathrm{blanc}} = c_{i,m}^{\mathrm{blanc}}\left(1 + \frac{\varphi_{\mathrm{IS}}}{\varphi_{\mathrm{blanc}}}\right) = c_{\mathrm{i},m}^{\mathrm{blanc}}(1 + \beta) \tag{S3}$$

$$c_i^{\mathrm{plasma}} = c_{i,m}^{\mathrm{plasma}}\left(1 + \frac{\varphi_{\mathrm{IS}}}{\varphi_{\mathrm{plasma}}}\right) = c_{i,m}^{\mathrm{plasma}}\left(1 + \frac{\beta}{\alpha}\right) \tag{S4}$$

$$c_j^{\mathrm{plasma}} = c_{j,m}^{\mathrm{plasma}}\left(1 + \frac{\varphi_{\mathrm{IS}}}{\varphi_{\mathrm{plasma}}}\right) = c_{j,m}^{\mathrm{plasma}}\left(1 + \frac{\beta}{\alpha}\right) \tag{S5}$$

with c_{m} being for the concentration measured at the GC.

The conversion of a single reactant is expressed in terms of the concentrations, defined in equation (S3) and (S4), and the correction factor α defined in equation (S1):

$$X_i = \frac{c_i^{blanc} - \alpha \cdot c_i^{plasma}}{c_i^{blanc}} = 1 - \frac{\alpha \cdot c_i^{plasma}}{c_i^{blanc}} . \quad (S6)$$

The total conversion is defined as the weighted average of the conversion for each reactant, weighted over their concentration in the inlet gas mixture:

$$X^{tot} = \sum_i c_i^{blanc} \cdot X_i . \quad (S7)$$

The specific energy input (SEI) and the energy cost (EC) are calculated according to equations S8 and S9, respectively:

$$\text{SEI (kJ/mol)} = (P * 60/Q_{in}) * V_m, \quad (S8)$$

$$\text{EC (kJ/L)} = \text{SEI (kJ/L)}/(X^{tot}/100\%) = (\text{SEI (kJ/mol)}/ V_m)/(X^{tot}/100\%), \quad (S9)$$

with *P* being the power delivered into the plasma (kW), Q_{in} the inlet, total flow rate in standard liters per minute (slm), 60 is the number of seconds per minute (s/min) and V_m the molar volume at atmospheric pressure and room temperature (24.5 L/mol).

2. Volumetric production rates

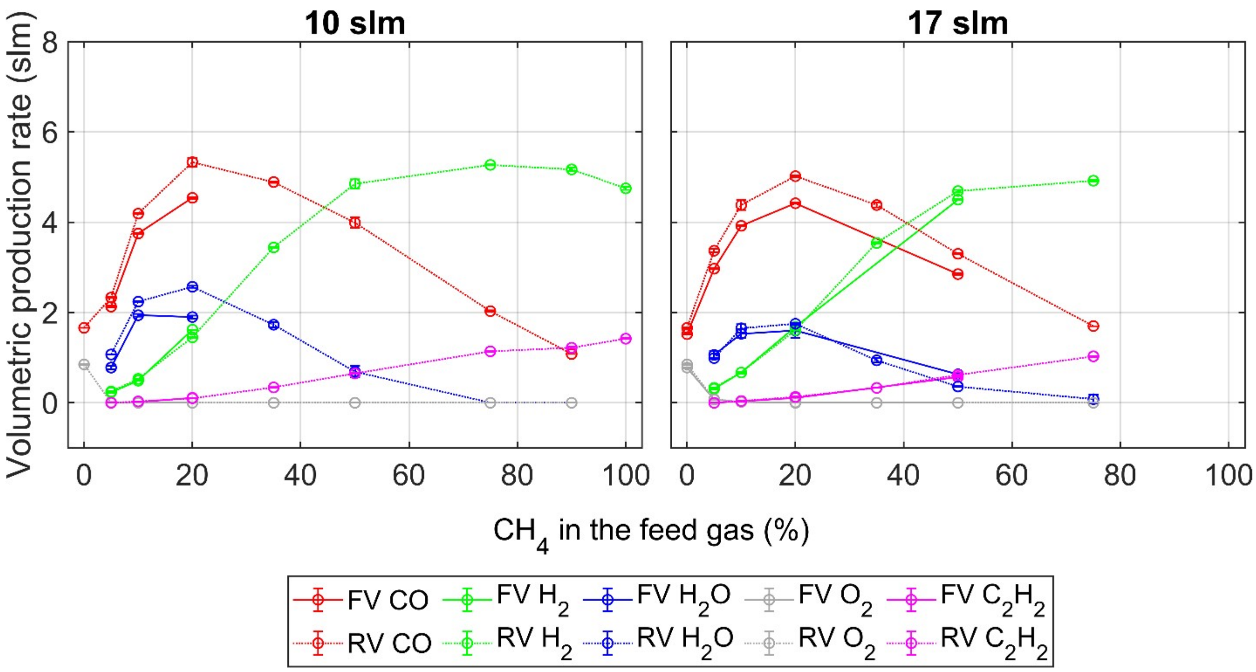

Figure S1. Volumetric production rate in standard liters per minute (slm), calculated by multiplying the product fractions with the output flow rate, for forward vortex (FV) and reverse vortex (RV) flow configurations at 10 and 17 slm input flow rate (1000 W, 100 mbar). The results exhibit similar trends to the product composition shown in Figure 8 in the main paper. Small differences can only be observed in CO and H_2O production. Furthermore, the volumetric production rates are very similar for 10 and 17 slm.

3. Estimation of the plasma size

Optical emission imaging is used to reconstruct the shape of the plasma, following the O 777 nm emission line intensity[3,4] with an image intensified CCD high-speed camera. The O 777 nm line emission is isolated with a bandpass filter with a central wavelength of ca. 780 nm. The resulting axial and radial profiles for the pure CO_2 microwave discharge at 17 slm are shown in Figures S2 and S3, respectively. Pure CO_2 is chosen to avoid interference from broadband emission of carbon particles, which may alter the estimated plasma dimensions. An accurate estimation of the plasma size upon addition of CH_4 goes beyond the scope of this analysis, which is meant only to provide an estimate of the timescale of core-periphery transport in reverse and forward vortex flow configurations.

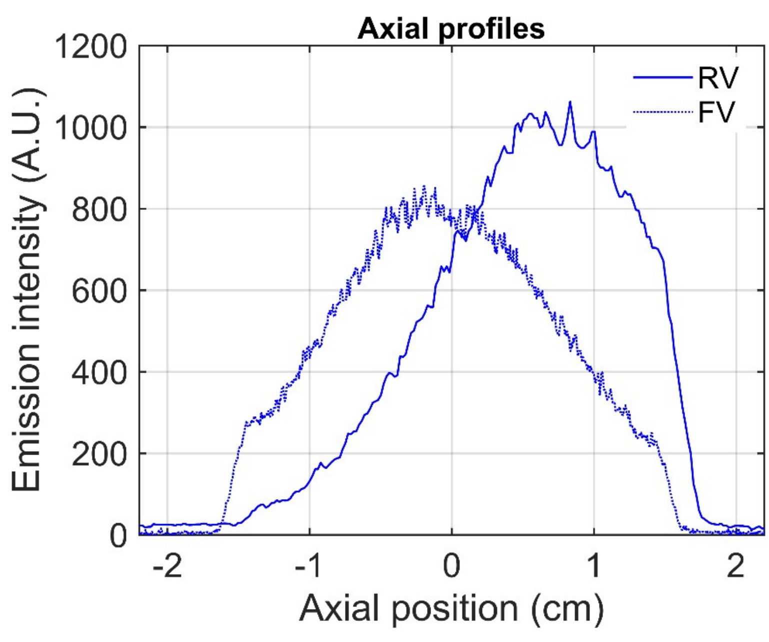

Figure S2. Axial profiles of the O 777 line emission intensity in reverse and forward vortex flow configurations (pure CO_2, 1000 W, 100 mbar, 17 slm).

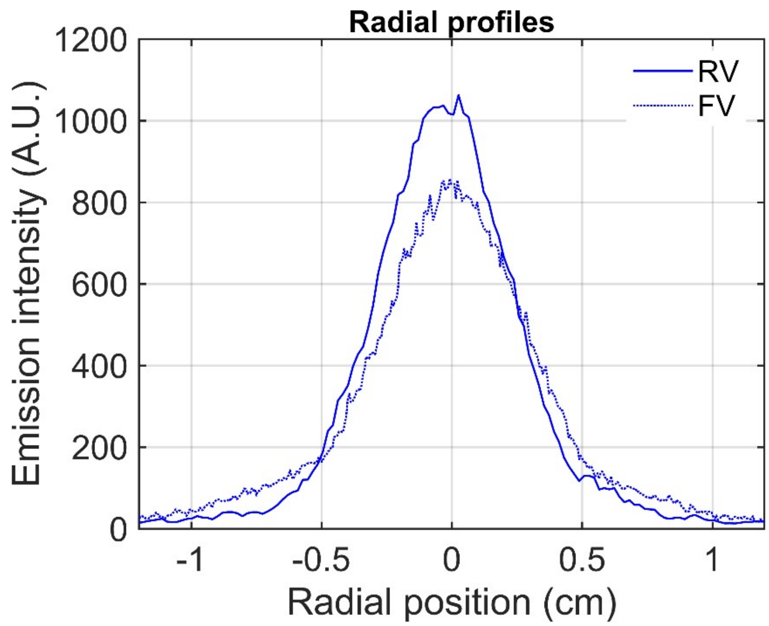

Figure S3. Radial profiles of the O 777 line emission intensity in reverse and forward vortex flow configurations (pure CO_2, 1000 W, 100 mbar, 17 slm).

Plasma length and width are calculated upon fitting of the O 777 line intensity (shown in Figure S2 and S3, respectively) with a Gaussian and defined as the full width at half maximum (FWHM) of the radial and axial profiles, respectively[3]. The resulting dimensions are reported in Table S1 and are used to estimate the characteristic gas residence time for the forward and reverse vortex flow configurations, reported in the main paper.

Table S1. Plasma length and width for pure CO_2, 1000 W, 100 mbar, 17 slm.

	Length (cm)	Width (cm)
Forward vortex	2.3	0.8
Reverse vortex	1.9	0.6

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