Supporting information: Plasma-based conversion of CO₂ and CH₄ into syngas: a dive into the effect of adding water

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S1. H₂O vapor input fraction as function of liquid H₂O temperature

As described in the main paper in section 2.1, dry gas (CO_2 and CH_4) is sent through the H_2O container surrounded by an oil bath, which is heated to a certain temperature. The amount of H_2O vapor carried with the dry gas flow towards the reactor inlet depends on this temperature. Table S.1 presents the mass of H_2O vapor per volume dry gas as taken from literature¹, as a function of temperature. The input fraction of H_2O vapor (in vol%) is then derived by converting the mass of H_2O per M_2O per wolume dry gas, taking into account the molar volume at 1 atm and the corresponding temperature.

Table S.1 – Mass of H_2O vapor per volume dry gas (kg/m³), molar volume at 1 atm (L/mol) and H_2O input fraction (vol%) as function of temperature (°C)

Temperature (°C)	kg H ₂ O/m³ dry gas	Molar volume (L/mol) at 1 atm	H₂O input fraction (vol%)
60	0.13	27.3	16.5
70	0.2	28.2	23.8
80	0.29	29.0	31.8
90	0.42	29.8	41.0
100	0.59	30.6	50.1

As a result, the relation between temperature and H_2O input fraction between 60 and 100 °C can be represented by a 2^{nd} degree equation (with $R^2 = 0.9999$):

$$H_2O$$
 input fraction = 3.3 x $10^{-5} \cdot T^2 + 0.0031 \cdot T - 0.14$

This equation is subsequently used to determine the exact H_2O input fraction and flow rate entering the reactor at the conditions under study in our work (see Table 1 in the main paper).

S2. Derivation of species molar output flow rates

As described in the main paper in section 2.1, the output gas mixture passes through a cold trap where the liquid fraction is condensed, and the dry gas mixture arrives at the gas chromatograph (GC) for analysis. The molar/volumetric fractions of these components are obtained through calibration prior to the experiments, but the molar flow rates of the individual species cannot be measured. For this reason, the total output molar flow rate needs to be derived, and together with the molar fractions measured at the GC, it leads to the individual species molar flow rates. In our case, the total output flow rate can be derived through assuming a perfect C-balance:²

$$1 = \frac{\dot{n}_{tot}^{out} \cdot \left(\sum_{i} \left(\mu_{i}^{C} \cdot y_{i}^{out}\right) + \sum_{j} \left(\mu_{j}^{C} \cdot y_{j}^{out}\right)\right)}{\dot{n}_{tot}^{in} \cdot \sum_{i} \left(\mu_{i}^{C} \cdot y_{i}^{in}\right)}$$

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In this equation i and j are representing reactants and products, respectively, and in and out are representing values corresponding to the reactor input or output, respectively. The total molar flow rate is noted as $\dot{n}_{tot}^{in/out}$, fractions measured with the GC are noted as $y_{i/j}^{in/out}$ and $\mu_{i/j}^{C}$ represents the number of C atoms in one molecule of i or j. As can be seen, when all carbon-containing components present in significant amounts are taken into account in this equation, the only unknown becomes the total molar output flow rate \dot{n}_{tot}^{out} .

The soot formed during measurements does not compromise this assumption, since for each condition labeled as green or orange, less than a mg was collected at the end of the measurement, i.e. the actual 'soot generation rate' expressed in mmol/min is negligible. Moreover, this approach is validated by comparing with a 500 mL soap film flow meter and stopwatch used with the initial measurements for a varying H_2O input fraction. In Table S.2 we present the difference in terms of dry output flow rate and corresponding residence time in the flow meter obtained through the two techniques. As can be seen, the time difference is max. 0.5 s, which is an acceptable deviation given the inevitable human error during measurements with a stopwatch while using the soap film flow meter. These measurements, together with the negligible amount of soot collected, demonstrate that the assumption of a carbon balance equal to 1 is generally acceptable.

Table S.2 – Comparison of the dry output flow rate and residence time of the output gas in the 500 mL soap film flow meter, derived through the carbon balance and measured with the actual flow meter, at a varying H_2O input fraction (%).

	28% H ₂ O input fraction		36% H ₂ O input fraction		45% H ₂ O input fraction	
	Based on C-	Based on	Based on C-	Based on	Based on C-	Based on
	balance	flow meter	balance	flow meter	balance	flow meter
Dry output flow rate (Ls/min)	3.358 ± 0.006	3.44 ± 0.05	3.069 ± 0.006	3.07 ± 0.04	2.700 ± 0.006	2.82 ± 0.04
Residence time flow meter (s)	8.93 ± 0.09	8.7 ± 0.2	9.8 ± 0.1	9.8 ± 0.2	11.1 ± 0.1	10.6 ± 0.2

Finally, note that the flow rate of unconverted H_2O at the outlet cannot be obtained through this approach as it does not arrive at the GC. However, in previous work the liquid fraction for DRM³ and OCRM⁴ in an APGD, at a similar SEI, was analyzed and the liquid by-products other than H_2O were negligible. We therefore assume that H_2O can be considered as the only product not detected by the GC, and hence the H_2O output flow rate can be derived from the mass balance equation, where it is the only unknow variable:

$$1 = \frac{\dot{n}_{tot}^{out} \cdot \left(\sum_{i} \left(M_{i} \cdot y_{i}^{out}\right) + \sum_{j} \left(M_{j} \cdot y_{j}^{out}\right)\right)}{\dot{n}_{tot}^{in} \cdot \sum_{i} \left(M_{i} \cdot y_{i}^{in}\right)}$$

With $M_{i/j}$ representing the molecular mass of i or j. The molar flow rates of all individual species are then used in the formulas described in section 2.2 in the main paper.

S3. Performance metrics at constant power and different current-voltage combinations

A slight decrease in power caused by soot formation can be counteracted by a small increase in either current or inter-electrode distance, which changes the voltage, so that the power goes back to its original level. Changing the inter-electrode distance would change the residence time of the molecules in the plasma. However, this was found not to affect the performance within a sufficiently wide range.

At a constant total input flow rate (3 Ls/min), total power (300 W) and gas composition (42-22-36 vol% CO_2 - CH_4 - H_2O), four different current-voltage combinations were tested, and the performance metrics remained virtually the same. Note that the inter-electrode distance at the highest current (ca. 28 mm) is almost half of the inter-electrode distance at the lowest current (ca. 52 mm), indicating that this is a sufficiently wide range tested, especially to validate only small changes during a regular experiment.

		40 mA – 11.5 kV	50 mA – 11 kV	60 mA – 11 kV	75 mA – 11.5 kV
Conversion (%)	CO ₂	46.4	46.9	45.8	47.0
	CH ₄	71.0	70.6	68.4	69.6
	H ₂ O	-13	-14	-14	-15
Yield (%)	СО	52.9	52.7	51.3	52.6
	H ₂	34	35	33	34
Syngas ratio		0.83	0.83	0.82	0.79
Energy cost (kJ/mol)	Conv based	450	460	480	460
	Syngas- based	225	226	230	230
Energy efficiency (%)		62	63	61	62

References

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