

# Supporting information: Enhancing CO<sub>2</sub> conversion with plasma reactors in series and O<sub>2</sub> removal

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## S1. Calculation of the conversion

In the case of pure CO<sub>2</sub> conversion, with the conversion  $\chi$ , the reaction goes as follows:

Table SI - 1 Reaction equation for pure CO<sub>2</sub> conversion

reaction	CO <sub>2</sub> →	CO	O <sub>2</sub>
in	1	0	0
out	1- $\chi$	$\chi$	$\chi/2$

Which means we calculate the measured concentrations (taking into account gas expansion) like this:

$$y_{CO_2} = \frac{1 - \chi}{(1 - \chi) + \chi + \frac{\chi}{2}} = \frac{1 - \chi}{1 + \frac{\chi}{2}}$$

$$y_{CO} = \frac{\chi}{1 + \frac{\chi}{2}}$$

$$y_{O_2} = \frac{\frac{\chi}{2}}{1 + \frac{\chi}{2}}$$

When using the  $\mu$ GC, the area of the CO<sub>2</sub> peak is used to calculate the fraction of reaction products:

$$y_{products} = y_{CO_{out}} + y_{O_{2out}} = \frac{A_{CO_2blanc} - A_{CO_2plasma}}{A_{CO_2blanc}}$$

This measured value should be related to the CO<sub>2</sub> fraction as follows:

$$y_{products} = y_{CO_{2in}} - y_{CO_{2out}}$$

In case of pure CO<sub>2</sub>, the inlet fraction equals 1, and we know the relation for the output concentration from the stoichiometry as in Table 1:

$$y_{products} = 1 - \frac{1 - \chi}{1 + \frac{\chi}{2}}$$

We can rearrange this equation to calculate the conversion:

$$\chi = \frac{2y_{products}}{3 - y_{products}}$$

This formula inherently accounts for the gas expansion.

## S2. Calculation of the gas expansion

To quantify the gas expansion, we calculate the O<sub>2</sub> concentration knowing that O<sub>2</sub> is 1/3 of the products:

$$y_{O_2} = 1/3 * y_{products}$$

Which can be applied to calculate the expanded volume flow rate as follows:

$$\Phi_{expanded} [L_n \text{ min}^{-1}] = \Phi_{initial} [L_n \text{ min}^{-1}] + y_{O_2} \cdot \Phi_{initial} [L_n \text{ min}^{-1}]$$

An alternative method is to work directly with the conversion. In the limit of full conversion ( $\chi=1$ ), the flow should expand with a factor 1.5:

$$\Phi_{expanded,direct} [L_n \text{ min}^{-1}] = \Phi_{initial} [L_n \text{ min}^{-1}] \cdot (1 + 0.5 \cdot \chi)$$

This results in a slightly higher expansion of the flow rate, but the difference between the two methods remains small. An overview of the difference magnitude is provided in table SI2.

Table SI - 2 Difference in the calculation methods for the gas expansion

$\Phi_{expanded} [L_n \text{ min}^{-1}]$	$\Phi_{expanded,direct} [L_n \text{ min}^{-1}]$	Difference $[L_n \text{ min}^{-1}]$	Difference (%)
1.027	1.040	0.014	1.33
1.049	1.074	0.025	2.38
1.067	1.101	0.034	3.22
1.082	1.125	0.042	3.91
1.095	1.144	0.049	4.44
1.104	1.158	0.054	4.85
1.112	1.169	0.057	5.15

### S3. Temperature in the reactor

As an estimation of the temperature in the reactor surrounding the plasma, we installed three temperature probes, as displayed in Figure SI1:

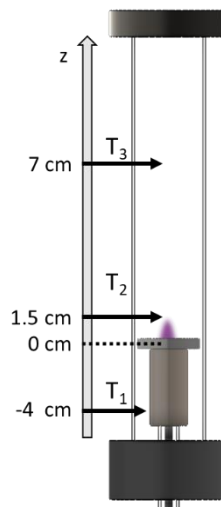


Figure SI - 1 Temperature probes installed in the reactor

Note that the anode is located at position  $z = 0$  cm,  $T_1$  is at  $z = -4$  cm close to the ceramic part,  $T_2$  at  $z = 1.5$  cm and  $T_3$  at  $z = 7$  cm. The  $T_2$  probe was the closest to the plasma and positioned in the afterglow, but contact with the discharge was avoided, since this would disturb the measurement. We tested the conditions of pass four and compared the temperatures of the three methods. The results are displayed in Table SI3:

Table SI - 3 Temperature measurements in the reactor (in °C)

pass 4	Standard	O <sub>2</sub> removal	O <sub>2</sub> addition
T <sub>1</sub> ceramic piece (°C)	86.3	83.4	82.9
T <sub>2</sub> afterglow (°C)	109.5	90.8	98.9
T <sub>3</sub> outlet (°C)	124.0	117.7	120.3

The temperature of  $T_2$  is lower than the temperature of  $T_3$ , because the gas flows in a vortex out of the anode and the hottest part might not reach the probe. The position of the probes was exactly the same in each test, so the results are still comparable. The temperatures in the reactor are not representative for the temperature inside the plasma, which is indeed much higher, so these are just a rough estimate to compare the discharge characteristics. Although it is difficult to draw firm conclusions, at least they can give us an indication of possible variations between the three different methods. In a different type of plasma reactor, not surrounded by a ceramic tube, *in-situ* experiments could help to determine the temperature in the plasma itself and provide more information on the effect of O<sub>2</sub> on the discharge characteristics. We can only conclude that the temperature in the reactor surrounding the plasma is similar for all three methods, so in first instance we assume that the temperature inside the plasma is also similar. Otherwise, we believe it would be reflected in the temperature of the afterglow. Since the power is also comparable for all three methods, we believe that the chemistry does play a crucial role in explaining the variations, and that the O<sub>2</sub> concentration influences the recombination reactions. In section 4, we place this in the context of literature. Especially in the work of Morillo-Candas *et al.* [1], the discharge characteristics are studied in more detail and their findings are in agreement with our own observations.

## S4. Performance in kWh/ton

To calculate the energy cost, we multiply the cumulative conversion with the total flow rate to obtain the conversion rate (in L/h). We divide this by the power (in kW) to obtain the conversion rate (L/h) at 1 kW. By multiplying with the molar mass of CO<sub>2</sub> (in kg/mole) and the molar volume (in mole/L), we get the mass flow rate (in kg/h per kW). Taking the inverse gives us the energy cost (in kWh/kgCO<sub>2</sub>), which is the energy needed to convert 1 kg of CO<sub>2</sub>. For industrial interest, we use this value in tonnes (kWh/ton). Finally, to make a better comparison with other technologies, it is interesting to look at the energy needed to produce one ton of CO. Therefore, we multiply the energy cost by the ratio of the molar masses (28/44) and obtain the energy cost for production (in kWh/tonCO). Both costs are summarised in Table S14.

Table S1 - 4 Cumulative conversion and energy cost for the single pass and four passes, for the standard method, O<sub>2</sub> removal and O<sub>2</sub> addition method

	Single pass	O <sub>2</sub> removal	Standard	O <sub>2</sub> addition
<b>Cumulative conversion (%)</b>	8.02	27.6	23.8	16.8
<b>Energy cost for CO<sub>2</sub> conversion (kWh/ton)</b>	7 379	8 761	9 383	12 056
<b>Energy cost for CO production (kWh/ton CO)</b>	11 595	13 768	14 745	18 945

This last value is most interesting to compare with other novel technologies for electrified CO production, as displayed in table S15.

Table S1 - 5 Comparison of ours work to the state of the art on electrified CO production

	kWh/t CO	Reference
Low temperature membrane electrode assemblies for electrolysis	6 100	[2]
H <sub>2</sub> shift electrolysis	6 000	[3]
Solid oxide electrolysis cell of Haldo Tropsch (with the theoretical binding energy, excluding heat losses)	3100	[4]
APGD reactor single pass	11 000	This work
APGD reactor in series with O <sub>2</sub> removal	13 000	This work

It is clear that CO production is still more expensive in our plasma reactor compared to other novel technologies. However, it was not the purpose of our work to demonstrate the best performance, but to illustrate the potential of placing plasma reactors in series, for gas recycling. The energy cost of plasma-based CO production can certainly be further improved by reactor design modifications. Furthermore, each of the other examples also has important disadvantages that are not taken into account in this production cost. Low temperature membrane electrode assemblies (LT-MEA) for electrolysis require a large initial investment and are expensive to operate. Start-up and shutdown are slow, while the cells can degrade and need to be replaced regularly. The hydrogen shift electrolysis has a high operating cost and depends on the hydrogen production, for which more sustainable production is not established yet. Solid oxide electrolysis cells (SOECs) on the other hand have both a high investment and operating cost and suffer from thermal stresses, cell degradation and corrosion. In many works on these electrolysis cells, the heat losses are not taken into account, which might result in a much higher production cost of CO compared to the theoretical value. However, as described in section 5 of the main paper, SOECs do show better durability when applied as a separation technique after the plasma instead of pure CO<sub>2</sub> conversion.

Compared to these issues, our plasma reactor has some key advantages that should not be overlooked. The start-up and shutdown of our reactor is fast (~ immediate) and shows potential to store intermittent renewable energy in chemical form. Thanks to the simplicity of the reactor design (without precious metals), the initial investment cost is also lower and the reactor is even applicable for other gas conversion reactions, such as dry reforming of methane. [5] This flexibility can be expanded to the process design: simple changes even on lab scale can tune the conversion and energy cost. By putting the reactors in series and controlling the oxygen concentration, the most favourable ratio for efficient product separation can be obtained, as discussed in Section 5 of the main paper.

## References

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