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Enhancing CO_2 conversion with plasma reactors in series and O_2 removal

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Abstract

In this work, we take a crucial step towards the industrial readiness of plasma-based CO_2 conversion. We present a stepwise method to study plasma reactors in series as a first approach to a recycle flow. By means of this procedure, the CO_2 conversion is enhanced by a factor of 3, demonstrating that a single-pass plasma treatment performs far below the optimal capacity of the reactor. Furthermore, we explore the effect of O_2 in the mixture with our flexible procedure. Addition of O_2 in the mixture has a clear detrimental effect on the conversion, in agreement with other experiments in atmospheric pressure plasmas. O_2 removal is however highly beneficial, demonstrating a conversion per pass that is 1.6 times higher than the standard procedure. Indeed, extracting one of the products prevents recombination reactions. Based on these insights, we discuss opportunities for further improvements, especially in the field of specialised separation techniques.

Keywords

Plasma; CO_2 conversion; atmospheric pressure glow discharge; oxygen removal; reactors in series; recycle flow

Highlights

- Enhanced CO_2 conversion by plasma reactors in series.
- Removing O_2 from the mixture greatly improves the CO_2 conversion.
- Promising process to combine with specialised separation techniques.

1. Introduction

Global warming is one of today's major challenges. The largest contributor to this problem is the generation of greenhouse gases by human activity, dominated by CO_2. [1] To minimize the consequences of climate change, a combined strategy is needed that cuts carbon emission and lowers the current high levels of CO_2 in the atmosphere. Indeed, carbon capture and utilization (CCU) is being increasingly investigated to convert CO_2 into value-added chemicals and fuels. [2] By transforming this waste gas into a renewable feedstock, CCU can decrease our dependence on fossil fuels, so that technology can advance according to the cradle-to-cradle principle. [3] In the context of electrification of the industry, several alternative technologies are being developed, including plasma technology. [4]

Plasma is an ionized gas, consisting of various molecules, radicals, excited species, ions and electrons. When a plasma is generated by applying an electric field, i.e. a gas breakdown, the electrons in the plasma are more efficiently heated by the applied electric power than the other species, thereby activating the gas molecules through electron impact reactions. Depending on the discharge state and parameters, a considerable amount of the energy input can be directed towards useful reactions like CO_2 splitting. [5] Since a plasma reactor is easily switched on/off, it has great potential to store intermittent renewable energy in chemical form. Other important advantages include the fact that it does not require scarce materials, and that it is scalable to the size of the energy market. [4]

Different types of plasma reactors have already been examined for CO_2 conversion. [4] Dielectric barrier discharges (DBD) have a simple design and operate at atmospheric pressure. They reach high conversion (up to 30%) but their energy efficiency is quite limited (5-10 %). [6, 7] Microwave plasmas reach much higher energy efficiencies (mostly at 50%, sometimes even 80-90%), yet typically only at reduced pressures. [8] Gliding arc reactors can overcome these disadvantages: they operate at atmospheric pressure with good energy efficiencies (around 30%). However, their conversion is restricted to 8-9% by the limited fraction of gas passing through the reactor. [9, 10]

Atmospheric pressure glow discharges (APGD) are gaining interest for fundamental studies, [11] for instance of the glow-to-arc transition, [11, 12] but also for applications like surface modification [13, 14] and gas conversion. [15, 16] They operate in a stable regime at low current (a few to a few tens of mA) and with a high voltage (a few to a few tens of kV). Trenchev *et al.* [17] investigated their performance for CO_2 splitting and obtained particularly promising results with a so-called confined APGD. It encapsulates the plasma zone in a high-temperature resistant ceramic material, to maximize the fraction of gas activated by the plasma. It reaches a conversion of 12.5% for an input power of 110 W (6.5 kJ/L), resulting in an energy efficiency of 26%. For an atmospheric DC plasma, these results are very promising, although further improvements are necessary to make it competitive with other emerging technologies.

There exist different strategies to enhance the performance for gas conversion. One of them is to further improve the reactor design, but this requires creative designs, modelling and extensive experiments to test the ideas. An alternative is to look at the process in general and find other solutions to well-known limitations, such as the limited residence time in the plasma or the recombination of the reaction products.

A limited residence time can be one explanation for a low gas conversion. Furthermore, non-ideal gas mixing can be a key contributing factor to the overall limited conversion. [17] Improvements to enhance the conversion include the implementation of a more confined electrode design [17] or elongation of the plasma. [18] An alternative is to install multiple reactors in series or to recycle the output gas flow, both common approaches in process design. [19] In the core Haber-Bosch process for example, the conversion of a single pass is low (<20%), but this is increased by recycling the unconverted products back into the reactor. [20] Another example is methanol synthesis from syngas: by carefully tuning the rate of recycled unconverted gas to the fresh feed gas, almost complete carbon conversion can be achieved. [21]

Even though these concepts of reactors in series and recycle flows are omnipresent in chemical industry, it is not commonly investigated for plasma reactors. Roohollah *et al.* [22] studied plasma reactors in series for benzene removal and could enhance the 55% removal efficiency in a single cycle to complete removal in four cycles. Regarding the cost of (not) recycling gas in a process, Martorell *et al.*[23] calculated the differences for their direct current (DC) arc-jet for the deposition of diamond films. Without recycling, 63% of the break-even production cost was caused by gas consumption, compared to 21% when recycling 85% of the flow. Other examples include argon recovery, [24] detoxification of gas [25-27] or water [28] and gas conversion to value-added products. [29-31] Concerning CO_2 conversion specifically, Li *et al.* [32] designed an interesting plasma-sorbent system for integrated CO_2 capture and conversion. They tested a system of parallel reactors for continuous operation, as well as reactors in series. Although the CO concentration showed no significant difference in their test cases, the reactors in series were clearly superior to suppress the CO_2 concentration below 1%, demonstrating the importance of process design once more. Semiokhin *et al.* [33, 34] also studied CO_2 plasma in a low pressure (100-500 Torr) silent electric discharge. The degree of dissociation first increased with the duration of gas circulation and then stabilised to a constant value. Furthermore, this plateau was reached much sooner for higher power inputs, compared to the slow increase at low plasma powers. These examples illustrate the benefit of investigating gas recirculation to optimise the residence time in the plasma. Clearly, investigating reactors in series and recycle flows is an important step towards up-scaling of plasma reactors for industrialisation.

Another limitation for the overall CO_2 conversion is the recombination of the reaction products:

$$CO + O_2 \rightarrow CO_2 + O \qquad \text{(R1)}$$

One way to prevent this reaction is by quickly cooling the gas, to quench the converted reaction products, though this is difficult to facilitate in reality. [35] Another strategy is to remove one of the reaction products of CO_2 splitting. Oxygen for example can be extracted by means of membrane technology [36] or an oxygen scavenger. [37-39] The contrary is studied as well: one can explore the reactivity of O atoms in the plasma and induce the reverse of reaction R1. Additional conversion is possible through reaction of vibrationally excited CO_2 molecules with these O atoms, as demonstrated by previous modelling [40] and experimental [41] studies. Hence, in combination with the recycling flow described above, the O_2 and O atom concentrations might be key to enhance the conversion.

In this work, we present a stepwise method to study APGD plasma reactors in series for CO_2 conversion as a first approach to a recycle flow. Furthermore, we apply varying oxygen concentrations in this method to explore the effect of oxygen removal on one hand, and oxygen addition on the other hand, related to the above reaction R1. To the best of our knowledge, this is the first work that reports such a straightforward procedure for plasma reactors to study the combined effect of a recycle flow and controlled O_2 concentrations that can be applied to any existing plasma reactor for CO_2 conversion.

The paper is structured as follows. First, we describe the general experimental set-up and method in section 2, including the procedure for varying the oxygen concentrations. The performance of the normal procedure is demonstrated in section 3, which is then compared to the oxygen removal and addition methods in section 4. A discussion about expanding these results to a conceptual industrial recirculation process follows in section 5. Finally, the overall conclusion is presented in section 6.

2. Methods

2.1 Experimental setup

The experimental setup is shown in figure 1. A cathode pin and an anode plate form the basis of the confined APGD reactor, both in stainless steel (Therma 310S). A Macor® tube completely surrounds the discharge region and cathode. The latter has a groove of ± 1 mm deep to allow the gas to enter the discharge zone and ensure an effective cooling of the cathode. At the end of the ceramic tube, the gas exits through the 5 mm opening in the anode plate, which is placed at 16 mm from the cathode tip. Trenchev *et al.* [17] described the behaviour of this plasma reactor in more detailed experiments and a computer model. They observed that the electron temperature is much higher than the gas temperature (i.e. 1.9 eV or 20 000 K compared to 2500 K) which indicates that the plasma is in thermal non-equilibrium.

A mass flow controller (Bronkhorst El-Flow Select) was used to insert CO_2 into the reactor, with a purity of 99.5% and without preheating the gas. The input flow rate was 1 L_n min^{-1}. Two more mass flow controllers (Bronkhorst El-Flow Select) were used for CO and O_2 to reproduce the output mixture. The plasma is ignited by a high voltage Technix DC power supply (maximum 30 kV and 40 mA). A 300 kΩ ballast resistor maintains the plasma in a glow regime. The initial start-up voltage is pre-set to 30 kV, then drops to ± 10 kV once the plasma is ignited, which is the voltage over the plasma and the resistor. This value and the set current of 25 mA can be read directly from the power supply. After the reactor, the outlet gas flows to an Agilent Micro gas chromatograph (μGC) for analysis.

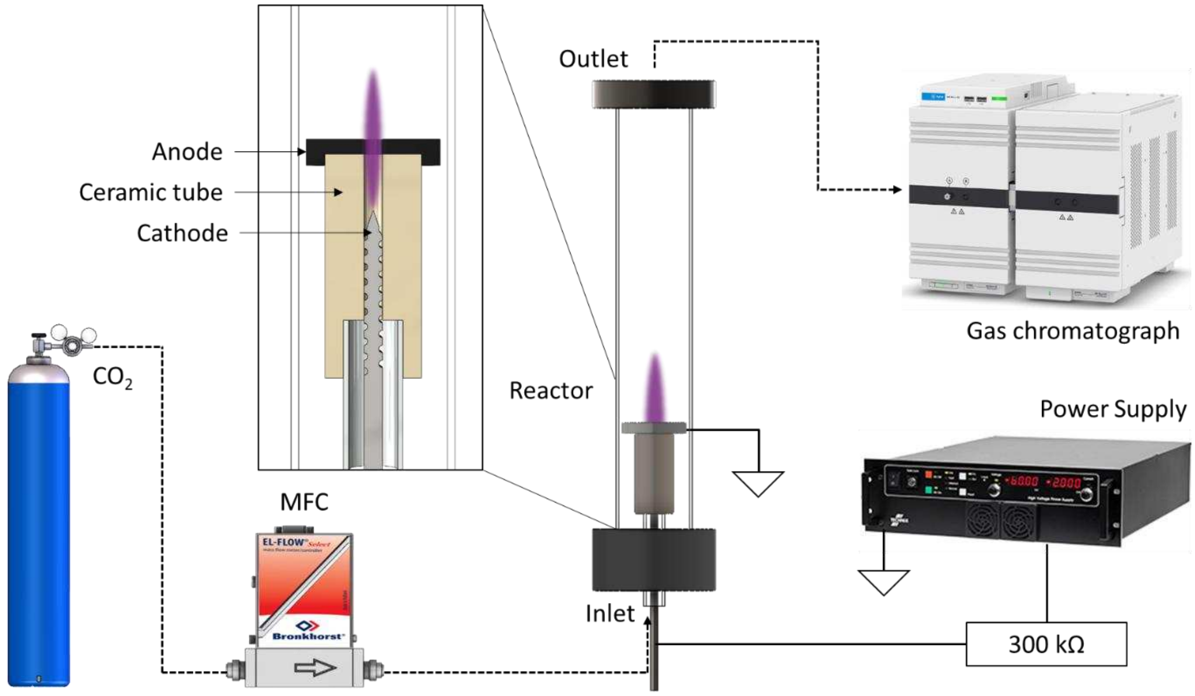

Figure 1 Schematic overview of the experimental set-up indicating the gas circuit (dashed lines) controlled by the mass flow controller (MFC) and the electrical circuit (full lines). The inset represents the inside of the reactor.

2.2 Gas analysis

When using the µGC, the following formula is used to calculate the fraction of reaction products:

$$\mathrm{y}_{\mathrm{products}} = \frac{\mathrm{A}_{\mathrm{CO_2(initial)}} - \mathrm{A}_{\mathrm{CO_2(out)}}}{\mathrm{A}_{\mathrm{CO_2(initial)}}} \tag{F1}$$

where $\mathrm{A}_{\mathrm{CO_2(initial)}}$ and $\mathrm{A}_{\mathrm{CO_2(out)}}$ are the initial and output areas of the CO_2 peak in the chromatogram. The initial CO_2 chromatogram is taken after the pure CO_2 gas passes through the reactor without plasma. The conversion is then calculated using the following formula (see derivation in Supporting Information (SI), section S1) [42, 43]:

$$\chi_{\mathrm{CO_2}}[\%] = \frac{2\,\mathrm{y}_{\mathrm{products}}}{3 - \mathrm{y}_{\mathrm{products}}} \cdot 100\% \tag{F2}$$

The specific energy input, an important parameter to determine the energy efficiency, is defined as:

$$\mathrm{SEI}\ [\mathrm{kJ\ L^{-1}}] = \frac{\text{Plasma power [kW]}}{\text{Flow rate } [\mathrm{L_n\ min^{-1}}]} \cdot 60\ [\mathrm{s\ min^{-1}}] \tag{F3}$$

With the flow rate expressed in L_n min^{-1} (liters normal per minute) with reference conditions at 20°C and 1 atm. The energy efficiency is defined as:

$$\eta\ [\%] = \frac{\chi_{\mathrm{CO_2}}[\%] \cdot \Delta \mathrm{H_R}{}^{\circ}[\mathrm{kJ\ mol^{-1}}]}{\mathrm{SEI}\ [\mathrm{kJ\ L^{-1}}] \cdot 24.1\ \mathrm{L\ mol^{-1}}} \tag{F4}$$

Where $\Delta \mathrm{H_R}{}^{\circ}$ is the reaction enthalpy for CO_2 splitting at standard conditions (i.e. 283 kJ mol^{-1}) and 24.1 L mol^{-1} is the molar volume defined at the same reference conditions of the flow rate (20°C and 1 atm).

Every experiment was performed three times, in order to apply a propagation of uncertainty to the results and calculate the error bars.

2.3 Procedure for reactors in series

We designed a stepwise method to study plasma reactors in series as a first approach to a recycle flow. The process is emulated in separate stages as represented in figure 2.

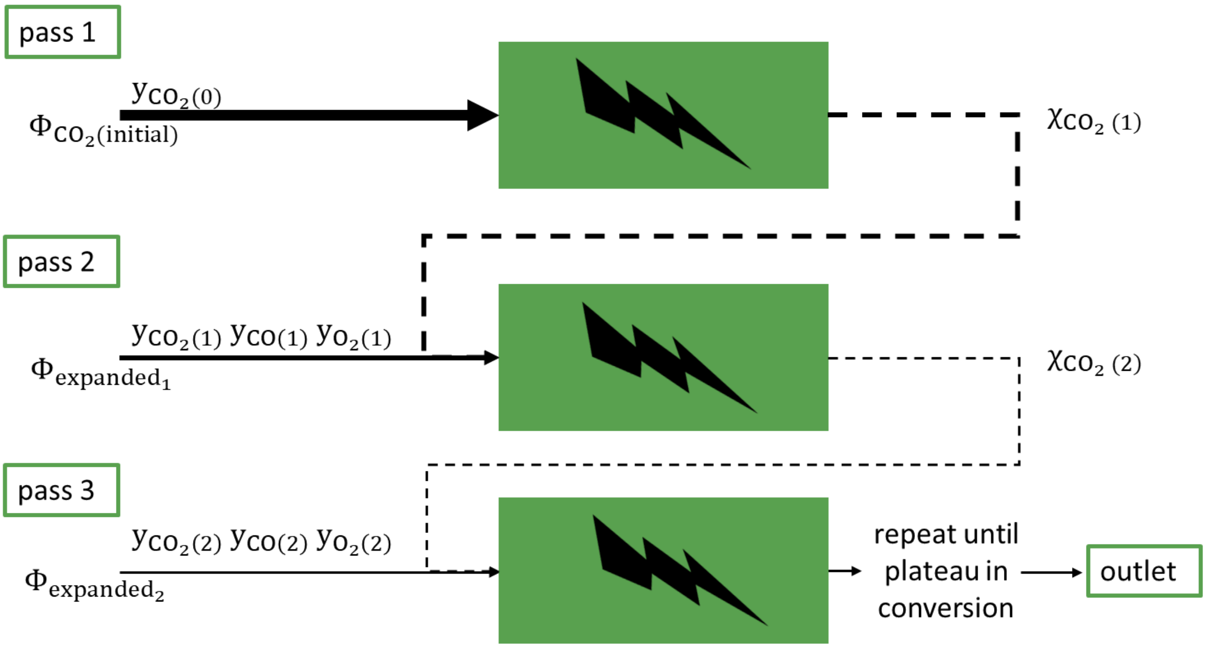

Figure 2 Schematic overview of the recirculation procedure. The first pass is a pure CO_2 plasma. The conversion χ and molar fractions y are determined in the mixture after the plasma to determine the concentrations in the next input mixture. The dotted lines represent the process that we replicate, while the full lines display the real input mixtures.

During the first pass, pure CO_2 gas flows through the plasma reactor. Inside the reactor, this CO_2 is partially converted into CO and O_2, which results in a lower CO_2 molar fraction $y_{CO_2(1)}$ after this first pass. From this, the conversion during the first pass (χ_1) can be determined with formula F2. Theoretically, it is known that the O_2 component is equal to the gas expansion. Hence, the expanded flow rate can be determined with this fraction (see derivation in SI, section S2):

$$\Phi_{\text{expanded}}[\text{L}_\text{n}\ \text{min}^{-1}] = \Phi_{CO_2(\text{inital})}[\text{L}_\text{n}\ \text{min}^{-1}] + y_{O_2} \cdot \Phi_{CO_2(\text{initial})}[\text{L}_\text{n}\ \text{min}^{-1}] \tag{F6}$$

With Φ_{expanded} the expanded flow rate in $\text{L}_\text{n}\ \text{min}^{-1}$ (litres normal per minute, at reference conditions 20°C and 1 atm), $\Phi_{CO_2(\text{initial})}$ the initial flow rate ($1\ \text{L}_\text{n}\ \text{min}^{-1}$) and y_{O_2} the O_2 fraction. Using this knowledge, the output mixture from pass 1 can be replicated as the input for pass 2 with the measured molar fractions:

$$\Phi_{CO_2(2)}[\text{L}_\text{n}\ \text{min}^{-1}\ ] = y_{CO_2(1)} \cdot \Phi_{\text{expanded}}[\text{L}_\text{n}\ \text{min}^{-1}\ ] \tag{F7}$$

$$\Phi_{CO(2)}[\text{L}_\text{n}\ \text{min}^{-1}\ ] = y_{CO(1)} \cdot \Phi_{\text{expanded}}[\text{L}_\text{n}\ \text{min}^{-1}\ ] \tag{F8}$$

$$\Phi_{O_2(2)}[\text{L}_\text{n}\ \text{min}^{-1}\ ] = y_{O_2(1)} \cdot \Phi_{\text{expanded}}[\text{L}_\text{n}\ \text{min}^{-1}\ ] \tag{F9}$$

With $\Phi_{i(j)}$ the flow rate in $\text{L}_\text{n}\ \text{min}^{-1}$ and $y_{i(j)}$ the molar fraction for each gas i after j passes through the reactor. We mix the gases with three mass flow controllers connected to their respective gas bottles, i.e. CO_2, CO and O_2, to replicate the exact output mixture (both the total flow rate and the ratio of its components). This forms the input mixture that we send to the plasma reactor for the next pass. The concentrations of this input mixture are measured without plasma ignition, to validate the above calculation. After the second plasma, this results in an even lower CO_2 fraction $y_{CO_2(2)}$ and a higher overall conversion χ_2 when compared to the initial blanc measurement of pure CO_2. The total product fraction is calculated with the area of the CO_2 peak after pass j through the reactor:

$$y_{\text{products,total}} = \frac{A_{CO_2(\text{initial})} - A_{CO_2(j)}}{A_{CO_2(\text{initial})}} \tag{F10}$$

$$\chi_{CO_2\ \text{total}}[\%] = \frac{2\ y_{\text{products total}}}{3 - y_{\text{products total}}} \cdot 100\% \tag{F11}$$

Note that (F10-F11) are very similar to (F1-F2) above, but apply now to the total product fraction and total CO_2 conversion. This procedure is repeated until the conversion stabilises. It practically simulates a system of identical plasma reactors in series, but can ultimately provide insight in the different stages of recirculation.

The specific energy input of the overall process is calculated similar to (F3) above, but the plasma power is multiplied with the number of passes j through the reactor. Next, the initial flow rate is used in this calculation, since these reactors in series treat the same initial gas volume:

$$\text{SEI}_{\text{total}}\ [\text{kJ L}^{-1}] = \frac{\text{j} \cdot \text{Plasma power [kW]}}{\Phi_{\text{initial}}[\text{L}_\text{n}\ \text{min}^{-1}]} \cdot 60\ [\text{s min}^{-1}] \tag{F12}$$

The total energy efficiency is then calculated as follows:

$$\eta_{\text{total}}\ [\%] = \frac{\chi_{CO_2\ total}[\%] \cdot \Delta H_R°[\text{kJ mol}^{-1}]}{\text{SEI}_{\text{total}}\ [\text{kJ L}^{-1}] \cdot 24.1\ \text{L mol}^{-1}} \tag{F13}$$

Where $\Delta H_R°$ and the molar volume are equal to the conditions in (F4).

2.4 Removal and addition of O_2

The above procedure is very flexible since we replicate the output of each plasma treatment by mixing CO_2, CO and O_2 from their respective gas bottles. This allows us to control the flow rates of each component and even adjust it, for example to study the effect of O_2 in the mixture. It should be noted that we assume ideal conditions for the calculation of the flow rates, but the detection of the output concentrations remains valid since the method of the µGC is independent of the flow rate.

In a second series of experiments, we mimic the procedure as if an oxygen scavenger would be present between each pass. The oxygen is arbitrarily removed by manipulating the input mixture, which implies that the gas flow rate stays equal to the initial flow rate since the expanded volume is removed. Then, the measured ratio of CO_2 and CO is maintained, so that the new input flow rates are calculated as follows:

$$\Phi_{\mathrm{CO_2}(j)}[\mathrm{L_n\ min^{-1}}] = \frac{\mathrm{y}_{\mathrm{CO_2}(j-1)}}{\mathrm{y}_{\mathrm{CO_2}(j-1)} + \mathrm{y}_{\mathrm{CO}(j-1)}} \cdot \Phi_{\mathrm{CO_2(initial)}}[\mathrm{L_n\ min^{-1}}] \tag{F14}$$

$$\Phi_{\mathrm{CO}(j)}[\mathrm{L_n\ min^{-1}}] = \frac{\mathrm{y}_{\mathrm{CO}(j-1)}}{\mathrm{y}_{\mathrm{CO_2}(j-1)} + \mathrm{y}_{\mathrm{CO}(j-1)}} \cdot \Phi_{\mathrm{CO_2(initial)}}[\mathrm{L_n\ min^{-1}}] \tag{F15}$$

With $\mathrm{y}_{\mathrm{i}(j-1)}$ the measured output fractions for each gas i from the previous pass $(j-1)$ through the reactor.

Finally, in the third series, we mimic the opposite from oxygen removal: after each pass, the O_2 concentration is doubled. The expanded flow rate is then calculated as follows:

$$\Phi_{\mathrm{expanded}}[\mathrm{L_n\ min^{-1}}] = \Phi_{\mathrm{CO_2(inital)}}[\mathrm{L_n\ min^{-1}}] + 2 \cdot \mathrm{y}_{\mathrm{O_2}} \cdot \Phi_{\mathrm{CO_2(initial)}}[\mathrm{L_n\ min^{-1}}] \tag{F16}$$

The new input flow rates are then calculated with twice the oxygen concentration:

$$\Phi_{\mathrm{CO_2}(j)}[\mathrm{L_n\ min^{-1}}] = \frac{\mathrm{y}_{\mathrm{CO_2}(j-1)}}{\mathrm{y}_{\mathrm{CO_2}(j-1)} + \mathrm{y}_{\mathrm{CO}(j-1)} + 2 \cdot \mathrm{y}_{\mathrm{O_2}(j-1)}} \cdot \Phi_{\mathrm{expanded}}[\mathrm{L_n\ min^{-1}}] \tag{F17}$$

$$\Phi_{\mathrm{CO}(j)}[\mathrm{L_n\ min^{-1}}] = \frac{\mathrm{y}_{\mathrm{CO_2}(j-1)}}{\mathrm{y}_{\mathrm{CO_2}(j-1)} + \mathrm{y}_{\mathrm{CO}(j-1)} + 2 \cdot \mathrm{y}_{\mathrm{O_2}(j-1)}} \cdot \Phi_{\mathrm{expanded}}[\mathrm{L_n\ min^{-1}}] \tag{F18}$$

$$\Phi_{\mathrm{O_2}(j)}[\mathrm{L_n\ min^{-1}}] = \frac{2 \cdot \mathrm{y}_{\mathrm{O_2}(j-1)}}{\mathrm{y}_{\mathrm{CO_2}(j-1)} + \mathrm{y}_{\mathrm{CO}(j-1)} + 2 \cdot \mathrm{y}_{\mathrm{O_2}(j-1)}} \cdot \Phi_{\mathrm{expanded}}[\mathrm{L_n\ min^{-1}}] \tag{F19}$$

With $\mathrm{y}_{\mathrm{i}(j-1)}$ the measured output fractions for each gas i from the previous pass $(j-1)$ through the reactor.

3 Performance of the APGD in series: CO_2 conversion and energy efficiency

We measured the CO_2 conversion and energy efficiency for a fixed initial flow rate of 1 Ln/min and a fixed input current of 25 mA, and the resulting power is in the range of 60-70 W. This power is lower than in the previous experiments of the APGD, [17] since we chose a shorter cathode-anode distance to ensure easy ignition. However, it was not the goal of this study to present the best results of this reactor, rather to demonstrate the principle of recirculation in a step-by-step procedure. The concentrations in the mixture after the plasma reactor are determined and then used as input for the next pass through the reactor.

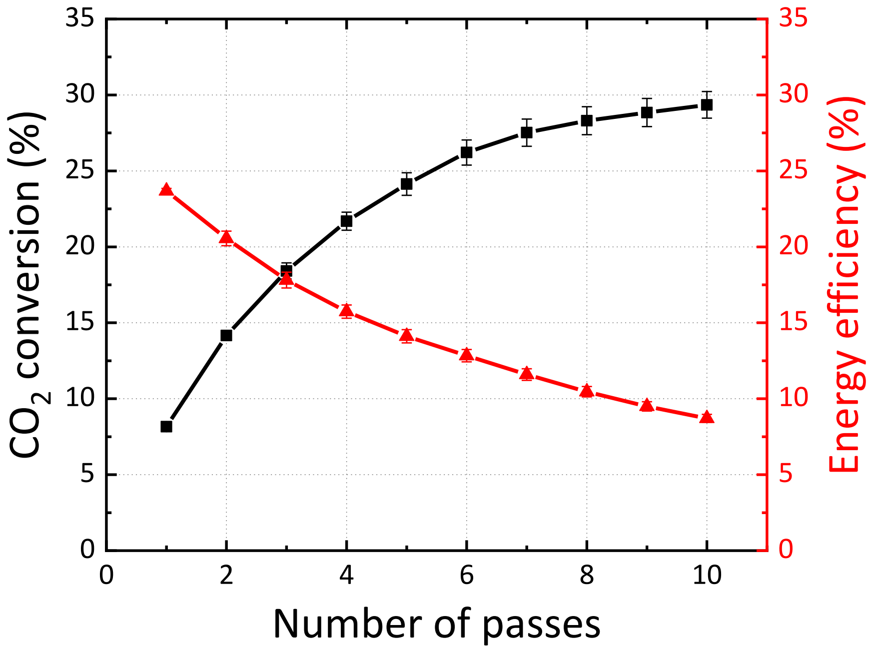

Figure 3 Evolution of the CO_2 conversion (left axis) and energy efficiency (right axis) for increasing number of passes through the reactor. The error bars indicate the deviation of the actual input concentration of CO_2 to the measured input CO_2 concentration, propagated to the energy efficiency. Some error bars are too small to be visible.

Figure 3 summarises the performance of the simulated reactors in series. The CO_2 conversion clearly rises from 8.16 ± 0.06% in the first pass to a threefold higher conversion of 24.1 ± 0.7 % in the fifth pass. The steep increase slows down to a plateau around eight passes, and to 29.3 ± 0.9 % in pass ten, which is 3.6 times the conversion of a single plasma treatment. The plateau in the CO_2 conversion indicates an equilibrium between splitting and recombination reactions, as discussed further in this work.

The energy efficiency drops simultaneously, since the same power is applied for a smaller additional conversion per pass. It is 23.7 ± 0.2 % for one pass, lowers to 14.1 ± 0.4 % in pass five, and further to 8.7 ± 0.3 % in pass 10. The trade-off between the conversion and the energy efficiency is clear. The first few passes are characterised by a rise in conversion with a limited drop in efficiency, e.g. in pass three the conversion is 18.4 ± 0.5 % with an efficiency of 17.8 ± 0.5%. The decline in the energy efficiency is more significant when the conversion starts to saturate, since the same power is applied for a smaller additional conversion per pass. Yet, the lower efficiency might be justified in certain processes. We observe a higher CO_2 conversion, which increases the CO concentration and thus the value of the output stream, thereby reducing the cost of the subsequent product separation. These type of experiments are very useful to design a process and balance these two performance parameters, as discussed in more detail in section 5.

The rise in conversion demonstrates that this plasma reactor performs far from its maximum capacity when applying a single plasma treatment. It is possible to apply this method to reactors with a higher conversion for a single plasma treatment, such as a DBD reactor. [6, 44] When starting from e.g. 15 % conversion, one might expect that the conversion saturates in less passes through the reactor. As indicated in the introduction [22-34], a variety of plasma reactors could benefit from reactors in series or a recycle flow, as well as a variety of gas mixtures including CO_2 with e.g. methane, hydrogen or nitrogen. Of course, the discharge characteristics for each reactor and gas mixture are different. Specific experiments are required to reveal possible improvements.

Reactors in series can increase the residence time in the plasma and one could expect an improvement similar to our results when elongating the discharge. However, only increasing the residence time might be insufficient if the same power is applied. Trenchev *et al.* [17] developed a model for the APGD studied in our work, which indicates that the chemical equilibrium is reached within 3 mm of the cathode tip along the axial coordinate ($r = 0$). The mixture maintains the same concentrations of species for the rest of the discharge length. Hence, simply increasing the plasma length would not improve the conversion. An alternative is to increase the plasma power, but this introduces two problems. First, atmospheric glow discharges are sustained at low currents to maintain a non-equilibrium and enhance the vibrational-induced dissociation pathway. When increasing this current, the plasma would reach thermal equilibrium and the conversion would become less efficient. [4] Second, higher powers might be difficult to realise in a certain setup. In our case, we chose a slightly shorter cathode-anode distance (to guarantee easy plasma ignition), which means our plasma volume was somewhat smaller than in [17]. The plasma was unstable when we increased the current, so we were limited in the input power. Reactors in series provide a solution for both of these issues. First, this method allows us to increase the energy input in the gas even when the power input in a single reactor is limited and second, it ensures the non-equilibrium, resulting in a higher overall conversion.

Our basic process is a general strategy to demonstrate the enhanced performance in existing reactors, which is exactly why these concepts are so widely applied in industry.

4 Oxygen removal and addition

4.1 Performance per pass

Instead of replicating the exact output mixture, we can also adapt the method to manipulate the O_2 concentration of the gas mixture inserted in the reactor. In this basic system, it is interesting to study the impact of either more or less O_2 in the mixture without the complications of implementing real oxygen scavengers. We measured the CO_2 conversion per pass and energy efficiency for a fixed initial flow rate of 1 Ln/min and a fixed input current of 25 mA, and the resulting power is in the range of 60-70 W.

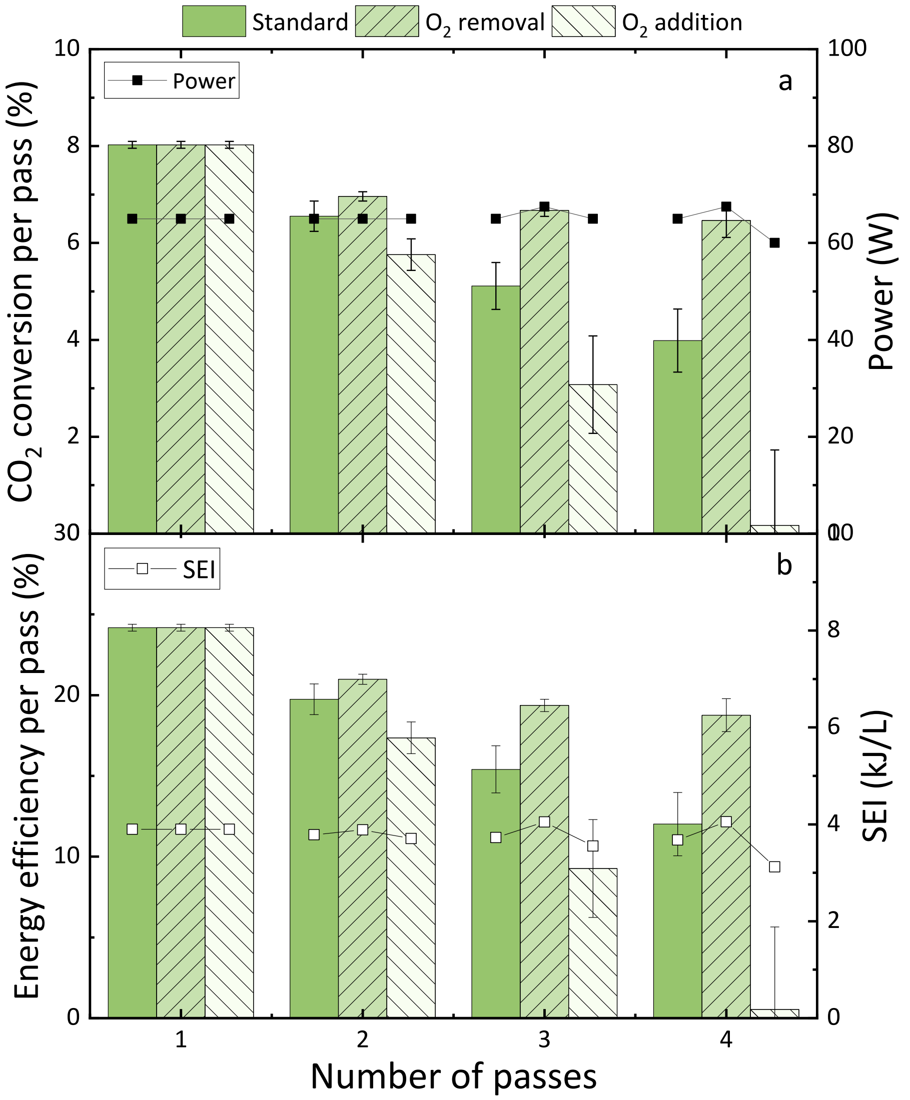

Figure 4 CO_2 conversion (a) and energy efficiency (b) per pass for the standard, O_2 removal and O_2 addition methods for four passes in total. The power (a) and SEI (b) for the different procedures are plotted as well, with the corresponding values indicated on the right y-axis. The error bars are quantified from the accuracy of the instrument and deviation between the theoretical and actual input CO_2 concentration for each new pass, propagated to the energy efficiency. In pass 1, the results of a pure CO_2 plasma are the same for all three methods.

There is a significant difference between the three methods, as shown in figure 4. The first pass through the reactor is a pure CO_2 plasma with a conversion of 8.02 ± 0.07 %, which is the same for all three methods. This is slightly lower than the result from section 3, since we operated at slightly lower powers (65 instead of 70 W). In the second pass, the differences start to appear and only become more obvious for a larger number of passes. The CO_2 conversion per pass of the standard method decreases to 3.99 ± 0.65 % in pass four. When O_2 is removed between the passes, the conversion per pass is higher and remains 6.47 ± 0.35 % in pass four, which is 1.6 times the conversion of the standard method. The opposite is true when adding extra O_2 in the mixture: the conversion per pass drops quickly to virtually zero (0.17 ± 1.56 %) in the fourth pass. For lower CO_2 concentrations (e.g. at higher conversions or when adding more O_2), the errors become larger on the CO_2 conversion and consequently on the energy efficiency as well. This might be related to the accuracy of the mass flow controllers, which were less suitable for lower CO_2 flow rates.

The energy efficiency shows similar trends. The first pass demonstrates an efficiency of 24.2 ± 0.2 % that drops to 12.0 ± 2.0 %, 18.7 ± 1.0 % and 0.54 ± 5.10 % in the fourth pass for the standard, O_2 removal and O_2 addition methods, respectively. It should be noted that these results disregard the energy cost related to removing or adding the oxygen in the mixture. In these experiments, there is no cost since we mix the components from the gas bottles in the lab. In a real process, such costs should be taken into account.

The O_2 removal clearly performs the best of the three methods. The conversion per pass stays nearly constant at ca. 6.5% in this case, resulting in a much better energy efficiency per pass (nearly 20%) than the other two methods and clearly outperforming the single pass result (an efficiency of 24% for only 8% conversion). Note that the efficiency shows the same overall trends as the conversion, since the SEI does not vary much between the methods. The physical conditions are indeed quite constant and only differ somewhat in the fourth pass, as shown in table 1. First, the flow accelerates and due to the chosen procedure, the O_2 addition method inherently leads to more expansion. Second, there is a small difference in power between the three procedures (7.5 W or 11% of the total). The same input current of 25 mA was maintained, but a slight change in the voltage was observed. This voltage drop across the plasma was calculated by subtracting the voltage drop over the resistor from the total voltage drop:

$$V_{plasma} = \frac{P_{total} - P_{resistor}}{I_{total}} = \frac{V_{total} \cdot I_{total} - R \cdot I_{total}^2}{I_{total}} \tag{F20}$$

With V_i the voltage (in V), P_i the power (in W), I_i the current (in A) and R the resistance (in Ohm) for the total circuit, plasma and resistor. For O_2 removal, the voltage drop increased slightly, indicating that the plasma becomes more resistive. For O_2 addition, the voltage drop decreased, showing that the plasma is slightly more conductive. Overall, this does not lead to a large change in power (which is at maximum only 7.5 W different between the three methods, as mentioned above; see Table 1). Third, the temperature in the discharge might be influenced by the changing O_2 concentration. Due to the confinement around the plasma, we could only measure the temperature in the reactor surrounding the plasma. Although these temperatures are not representative for the temperature inside the plasma, which is much higher, at least the temperatures in the reactor can give us an indication of possible variations between the three different methods, i.e. the standard method, O_2 addition and O_2 removal. They allow us to verify whether the latter would also affect the different results. We found that these temperatures are comparable for all three methods, as discussed in the SI (section S3). To conclude, we observe that the physical characteristics remain similar, while the change in O_2 concentration does affect the conversion greatly. Therefore, we believe that the chemistry plays a significant role, as will be discussed in the next section.

Table 1 Overview of the input conditions in pass 4 for each method

pass 4	Flow rate (Ln/min)	I_{total} (mA)	V_{plasma} (kV)	P_{plasma} (W)
Standard	1.073	25	-2.6	65
O_2 removal	0.998	25	-2.7	67.5
O_2 addition	1.198	25	-2.4	60

4.2 Cumulative performance

The total conversion cannot be determined with formula F12, since the CO_2 concentration is manipulated artificially in the O_2 procedures. An alternative is to take the sum of the conversions in each pass and evaluate this cumulative conversion, as shown in figure 5. For the energy efficiency, it is not straightforward to take the cumulative value, since the flow rate in the SEI value is manipulated artificially as well. Instead, we will compare the energy cost in this section.

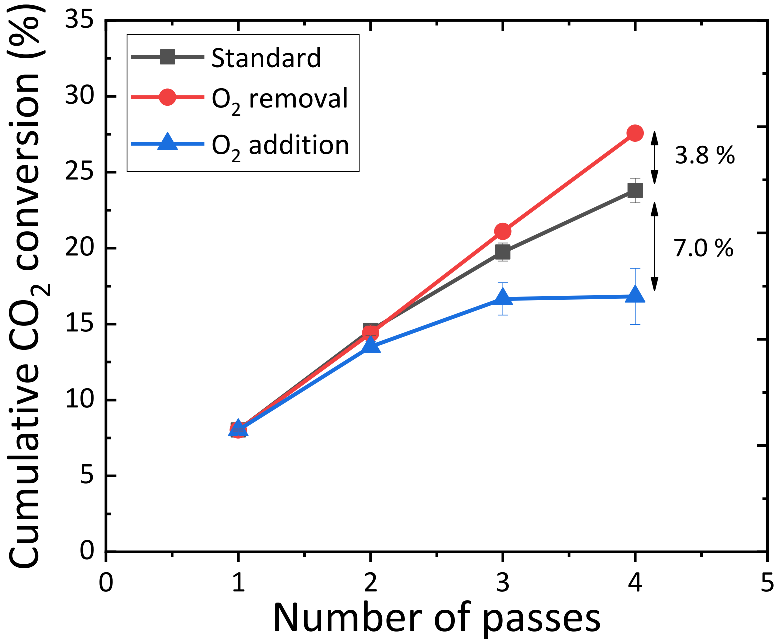

Figure 5 The cumulative CO_2 conversion of the standard, O_2 removal and O_2 addition methods for 4 passes in total. The difference in the final pass is indicated with arrows.

This comparison in figure 5 further highlights the significant difference in performance between the three methods. O_2 removal upon recirculation reaches the highest cumulative CO_2 conversion of 27.6 ± 0.4 % after four passes, followed by the standard method with a cumulative conversion of 23.8 ± 0.8 % and a substantially lower 16.8 ± 1.9 % cumulative CO_2 conversion for the O_2 addition method. All three procedures clearly surpass the single pass result of 8.02%. When removing O_2, the cumulative conversion is even more than 3 times higher than for the single pass.

Considering the power input and conversion rate for each pass, we can calculate the energy cost for this conversion, as explained in the SI (section S4) and summarised in table 2. Obviously, because of the lower power applied, the single pass method has the lowest energy cost (7 379 kWh/ton), although this is obtained for a significantly lower CO_2 conversion. The O_2 removal method, in spite of the much higher total power applied, requires 8761 kWh/ton, hence just 1 400 kWh/ton more. Indeed, the conversion is more than three times higher than in the single pass reactor for only a slightly higher energy cost, demonstrating the great potential of this method. Again, we should make a balance between CO_2 conversion and energy requirements, but it looks like gas recycling with O_2 removal leads overall to a better performance. A comparison with other technologies for CO_2 conversion is made in the SI (section S3). Please note that these results disregard the energy cost related to removing or adding oxygen in the mixture.

Table 2 Cumulative conversion and energy cost for the single pass and four passes, for the standard method, O_2 removal and O_2 addition method

Recycling stages	1 pass	4 passes		
Gas mixture	Standard	O_2 removal	Standard	O_2 addition
Cumulative conversion (%)	8.02	27.6	23.8	16.8
Total power (W)	65	265	260	255
Energy cost (kWh/ton)	7 379	8 761	9 383	12 056

These results demonstrate that O_2 has a clear detrimental effect on the CO_2 conversion. Due to the addition of a reaction product, the chemical balance shifts towards the synthesis of CO_2 instead of the dissociation and favours recombination reactions. This observation is in agreement with previous results of CO_2 plasmas at atmospheric pressure. Zhang *et al.* [45] observed a drop in conversion from 16.1 to 11% upon adding 20% or more O_2 in a packed bed DBD reactor. Indeed, while our O_2 concentration is as high as 34% in the fourth input mixture in case of the O_2 addition method, it is much lower in the standard method (9.5%) and virtually zero (0.007%) in the O_2 removal method. In another packed bed reactor, Navascues *et al.* [46] obtained a similar effect at lower O_2 concentrations. Their CO_2 conversion decreased from 13 to 8.5 % when adding only 10% O_2. Uytdenhouwen *et al.* [47] even ignited a mixture of 2/3 CO and 1/3 O_2 in a packed bed DBD, and found that this composition reached the same equilibrium as a pure CO_2 plasma, thereby proving the importance of this recombination reaction. These observations are not limited to atmospheric pressure plasmas only, Morillo-Candas *et al.* [48] studied CO_2-O_2 and CO-O_2 gas mixtures in a pulsed radio-frequency discharge. Their results also demonstrated a key role for O_2 in the recombination, more specifically in reaction with the excited state of CO. An enhanced CO_2 dissociation would be possible through the reverse of reaction R1, but for this, O atoms are needed, and thus the O_2 molecules would first need to undergo dissociation. This is apparently not the case in our conditions, and the O_2 molecules seem to contribute primarily to the recombination reaction with CO, leading to more CO_2.

Multiple studies investigated this balance on a more fundamental level: enhanced CO_2 conversion by the O-CO_2 association on one hand, and its competition with the CO and O_2 recombination on the other hand. When the enhanced CO_2 conversion upon reaction with O atoms happens in the afterglow, this mechanism is called super-ideal quenching, as investigated by Vermeiren *et al.*[35] Van de Steeg *et al.* [41] also demonstrated the importance of O-CO_2 association experimentally in a MW plasma at 60-120 mbar and high temperature (>3500 K), which contributed to 45% of the CO production. Furthermore, an extensive computational study by Berthelot *et al.* [40] gives insight in such a MW plasma under various conditions. On one hand, the reaction of CO_2 with O atoms contributed significantly at lower pressures and temperatures to enhance the CO_2 dissociation. On the other hand, at higher pressures (up to 1 bar) and certainly at higher temperatures (i.e. 3000 K), the recombination reaction of O_2 and CO became equally important. The authors suggested that an equilibrium is reached, which limits the CO_2 conversion at higher temperature and atmospheric pressure. Vargas *et al.* [49] later confirmed the importance of this reaction for the dissociation and recombination mechanisms. Morillo-Candas *et al.* [50] investigated the role of O atoms experimentally. They argued that adding O_2 to the mixture gives little insight in the role of O atoms, since these mixtures might also change other relevant plasma parameters, such as the CO density. Therefore, they inserted a material with a large specific surface area in a DC glow discharge at reduced pressure, causing O atoms to recombine into O_2 on the surface. The vibrational excitation of both CO_2 and CO increased at these conditions with a low O atom density, proving its role as a vibrational quencher. Interestingly, the CO_2 dissociation remained the same. This implies that vibrational excitation does not contribute to the dissociation on one hand, and that the back reaction mechanism does not involve O atoms on the other hand, confirming the importance of molecular O_2 for recombination, as observed in their previous work. [48] The role of O atoms as a vibrational quencher was observed earlier by Cerner *et al.,* [51] but not with lower O atom concentrations in the conditions of van de Steeg *et al.* [52]

Ultimately, the plasma conditions determine the role of molecular O_2 and O atoms in recombination and dissociation mechanisms. In our conditions, the O atom fraction is possibly too low to enhance CO_2 dissociation, due to recombination of O atoms to molecular O_2. When adding O_2 molecules to the CO_2 plasma, it is clear that the recombination reactions are dominant and reduce the conversion compared to a pure CO_2 plasma.

On the contrary, the removal of O_2 molecules is clearly more beneficial in our conditions. Le Chatelier's principle seems to hold true, even though a plasma is not necessarily in chemical equilibrium. Removing one of the reaction products will concentrate CO_2 in the mixture and shift the chemical balance to the reaction products, which was also studied in MW plasmas by Wolf *et al.* [53] Furthermore, when O_2 is actively removed, it cannot recombine with CO into CO_2 (reaction R1), which can explain the further rise in CO_2 conversion. The single pass conversion of 8.02 % rises to 27.6 % cumulative conversion, a factor 3.4 higher, while the energy efficiency in the fourth pass is still 18.7 %. It might be challenging to separate O_2 in the reaction mixture itself, as discussed in section 5 below, but again a recirculation procedure can provide a more flexible system to separate the molecules in between the passes.

5 Conceptual CO_2 recycling system

Our experiments are a first approach to study the potential of recirculation and allow a great flexibility to investigate the effect of various O_2 concentrations in the input gas mixture. However, our basic setup rather mimics the situation of multiple reactors in series than a recycle flow. More advanced systems in a single reactor are sometimes preferable in an industrial setting. The general scheme in figure 6 gives an overview of such a single reactor recirculation system.

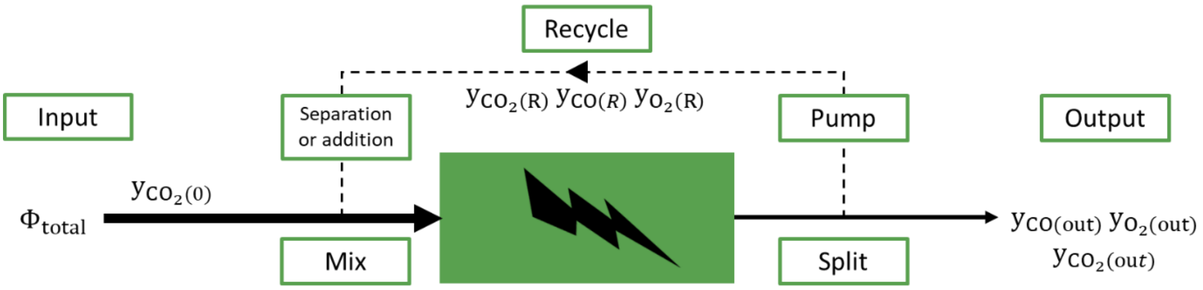

Figure 6 General scheme for a single reactor recirculation system. The input consists of CO_2 which flows through the plasma reactor. The outlet stream can be controlled by a pump to recycle a certain fraction (with or without separation/addition of certain components) back into the input stream.

Such a process requires only one reactor unit, but the integration and optimisation of the recycle flow is less straightforward than for reactors in series (where the number of passes relates directly to the CO_2 conversion and energy efficiency). The recycle ratio must be carefully tuned to obtain a good balance between CO_2 conversion and energy efficiency, which is decisive for product separation. [54] Depending on the process, it might be important to reach the highest CO_2 conversion possible to obtain a more favourable ratio for efficient product separation. On the contrary, the energy efficiency also plays a crucial role: the additional conversion might cost more than adapting the separation process.

Efficient product separation is undoubtedly an essential step for industrial application. [54] It is in fact the dominant cost factor, considering the separation of CO and O_2 is rather energy-intensive, as calculated by van Rooij *et al.*, [55] and the purity of the CO product determines the final selling price. This further highlights the relevance of separation systems in the recycle flow itself. Not only did we observe a significantly higher CO_2 conversion upon removing the oxygen in the recirculation flow, thereby increasing the CO concentration and thus the value of the output stream, this additional separation step could facilitate the final product separation, hence reducing the energy consumption for the same purity.

Traditional separation methods, such as pressure swing adsorption, are certainly applicable for the exhaust of plasma reactors. Carbajo *et al.* [56] investigated the use of commercial zeolite materials for typical $CO_2/CO/O_2$ mixtures. Indeed, high purity (> 96 %) and high recovery yields (> 97 %) are demonstrated for both CO and O_2.

Some novel separation techniques are also developed specifically for plasma reactors. One option to extract O_2 from the plasma, is to insert a hollow fibre membrane in the reactive gas, as investigated by Chen *et al.*[36] They obtained a clear synergistic effect when combining the two: the O_2 permeation flux through the membrane was improved by almost a factor of three in the CO_2 plasma compared to the same hollow fibre without the plasma. Buck *et al.* [57] also observed a higher O_2 permeation flux with the fibre in a plasma compared to heating in an electrical oven. These hollow fibres might be an interesting alternative to conventional non-plasma separation techniques, although direct contact between the plasma and the fibre might not be possible for all types of plasma reactors (depending on the temperature or arcs that might destroy the fibres). Another option is to combine a plasma with a solid oxide electrolysis cell. Pandiyan *et al.* [58] simulated the typical exhaust of a CO_2 plasma and supplied this to a high temperature electrolyser to enable electrochemical separation of the products. Indeed, oxygen can be separated from the product stream at relatively low temperatures (< 650°C) while CO production is increased via CO_2 electrolysis. Furthermore, the electrode stability is much better compared to the conventional CO_2 electrochemical conversion. In-situ plasma-SOEC reactors show promising results as well, [59, 60] although this is not applicable for all types of plasma reactors depending on the required temperatures, plasma properties, etc.

Another novel approach for product separation is the combination of a plasma with a carbon (charcoal) bed, as recently investigated by Girard-Sahun *et al.* [39] for a gliding arc plasmatron (GAP) reactor. They managed to enhance the CO_2 conversion by almost a factor two, while the CO concentration in the output even increased with a factor three, attributed to carbon gasification. Simultaneously, O_2 was completely removed from the exhaust. Huang J. *et al.* [37] obtained similar improvements with biochar, a more sustainable alternative to charcoal. Thermal plasmas perform even better, as demonstrated by Li Z. *et al.* [38] All these examples with charcoal for separation have the advantage that they require less energy for separation compared to traditional approaches such as pressure swing adsorption. Aside from a system to supply the (bio)charcoal, no extra gas flows or compression are required. Using such a carbon bed in combination with a gas recycling system is very promising indeed.

Other strategies to steer the reaction products include the addition of a hydrogen source (i.e., chemical in-situ oxygen trapping) [61] or plasma catalysis, [62] both growing research fields on their own. In general, it is more interesting to perform plasma catalysis on gas mixtures with a complicated mixture of reaction products, like dry reforming of methane (DRM). [62] These methods could produce value-added chemicals like formic acid and methanol in a single step, thereby skipping the separation step of pure CO_2 splitting altogether. For the APGD reactor studied in this paper, DRM performed well in previous experiments by Wanten *et al.* [16]. The combination with a catalyst could further increase the conversion and steer the product distribution, which will be subject of future research.

Aside from product separation, the presence of impurities in the input gas mixture should be taken into account when targeting industrial application. Depending on the specifics of the industrial application, this could present extra costs if extra separation steps before or after the plasma process are required. On the contrary, it could also provide a route for further optimization. The presence of N_2 in the gas mixture for example could enhance the performance of CO_2 conversion, as demonstrated by Snoeckx et al. in a DBD [42] and by Ramakers *et al.* in a gliding arc plasmatron. [63] In the DBD, N_2 enhances the CO_2 conversion for a similar energy efficiency if the N_2 concentration is below 50% N_2, resulting in a better overall conversion. In the gliding arc plasmatron, the CO_2 conversion increased from 5 to 18 % while forming interesting products like NO and NO_2 as basis for fertilizer (albeit too low for valorisation), without producing the greenhouse gas N_2O.

Another common impurity is water from a combustion process. The CO_2 conversion drops when adding even a few percent of H_2O in the mixture in most plasma processes. [4] Yet, the presence of water might be an incentive to perform the promising reaction called bi-reforming of methane (BRM). It was proposed by Olah *et al.* [64] to combine dry and steam reforming, in order to deliver an ideal syngas ratio in a single step, facilitating subsequent processing to methanol or the Fischer-

Tropsch synthesis. The inherent drawbacks of conventional catalytic BRM (slow start-up and catalyst deactivation) are no issue for plasma processes and will be the topic of future research.

It should be noted that our approach is still far from real industrial application, as it does not yet account for separation (costs), the effect of impurities and upscaling. However, we do believe that our results can already provide more insight for future industrial application of advanced plasma processes. Although we did not perform a techno-economic analysis, our simplified procedure reveals the opportunities of plasma in engineering and possible industrialisation. Further improvements in e.g. reactor design, heat recovery and plasma catalysis can strengthen the role of plasma technology as a valuable part of the CCU landscape.

6 Conclusion

In this work, we developed a basic procedure to study a plasma reactor (i.e. an APGD) in series as a first approximation of a recycle flow. The CO_2 conversion rises considerably with five passes (from 8% to 24 %) for a limited drop in energy efficiency (from 24 % to 14 % in pass five). Around 8-10 passes, the conversion saturates due to the competition between dissociation and recombination reactions, at a value of 29 % which is 3.4 times higher than the single pass. The energy efficiency decreases with each pass, since the same plasma power is applied for a smaller extra conversion per pass. Still, our procedure clearly outperforms the single pass conversion for reasonable energy efficiencies. It provides an alternative to increasing the energy input in the existing reactors, while maintaining the advantages of a non-equilibrium plasma at low current to improve the performance.

Thanks to the flexibility of our method, we were able to explore the reactivity of O_2 molecules: on one hand, O atoms can enhance the CO_2 dissociation (by the reaction: $O + CO_2 \rightarrow CO + O_2$), but on the other hand, O_2 molecules can recombine with CO and reduce the CO_2 conversion (opposite reaction). At our conditions, adding oxygen to the mixture has a detrimental effect on the CO_2 conversion, indicating it reacts as O_2 and not as O atoms. Instead removing the O_2 in between each pass has a clear beneficial effect, since removing a reaction product prevents recombination reactions and shifts the chemical balance to facilitate dissociation. The conversion per pass stays nearly constant, resulting in a much better energy efficiency per pass (nearly 20%) than the other two methods. The cumulative conversion of the O_2 removal method is nearly 28 % after four passes, and thus, more than three times higher than the 8 % of a single pass. Obviously, this comes at a somewhat higher energy cost, because a higher total power is applied in the recirculation method. However, while the single pass method exhibits an energy cost of 7380 kWh/ton, the O_2 removal method requires only a slightly higher energy cost of 8760 kWh/ton. Although we did not account for the cost of separation yet, these results still demonstrate the great potential of this method.

In conclusion, a recycle flow in plasma reactors is highly promising, especially when removing the $_{O2}$ with separation strategies such as pressure swing adsorption, hollow fibre membranes, solid oxide electrolysis, or the combination with a carbon bed to extract the O_2. This work reveals interesting opportunities for the industrialisation of plasma processes and its potential to be a valuable part of all CCU technologies that are necessary for the transition to a more sustainable world.

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