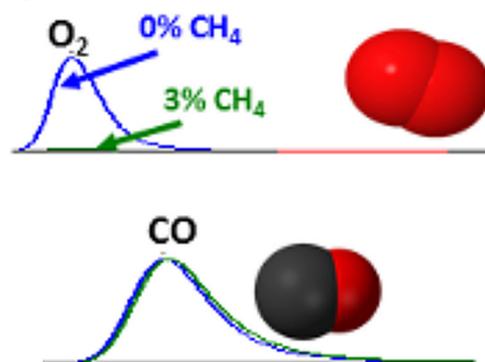


In-Situ Chemical Trapping of Oxygen in the Splitting of Carbon Dioxide by Plasma

Robby Aerts,* Ramses Snoeckx, Annemie Bogaerts*

A crucial step in the plasma splitting of carbon dioxide is the separation of the conversion products, and this is not straightforward, especially for separating O_2 from CO_2 and CO . In this work the trapping of atomic oxygen by adding a hydrogen source, which enhances the chemical conversion into water, is demonstrated. The experimental and modelling results show that by adding 3% of H_2 and 2% of CH_4 most of the oxygen can be trapped at a CO_2 conversion of $\pm 2.5\%$. The identified products formed by the addition of CH_4 or H_2 are mainly H_2O and in the case of CH_4 also H_2 . Adding a hydrogen source thus leads to the removal of O_2 , leaving behind a gas mixture that can be more easily separated.



1. Introduction

Reducing CO_2 emissions is one of the key pillars for a shift towards a sustainable green economy. One way to achieve this, and at the same time use the CO_2 as a chemical feedstock, is carbon capture and utilization (CCU). This technology is already widespread. It includes both the direct use of CO_2 , for example, as a solvent, as well as the chemical or biological conversion of CO_2 into more valuable chemicals.^[1]

One possible chemical conversion pathway is CO_2 splitting (into O_2 and CO) by plasmas. This technology has already demonstrated high energy efficiencies^[2,3] and can also be used in combination with a catalyst to enhance the energy efficiency or the selectivity of the process.^[4]

At the same time, the large scale adoption of renewable energy sources poses a challenge regarding efficient storage and easy transport of the electricity produced (i.e., during peak moments on the grid). The most efficient solution appears to be chemical storage in fuels.^[5] Since fuels offer a much higher gravimetric and volumetric energy storage capacity, they have much higher energy densities than electrical storage techniques and they match the existing

worldwide liquid fuel infrastructure.^[5,6] As such, the current transition to renewable energy sources does not only give plasma processes a clean electricity source, but because of the high operation flexibility, plasmas can be turned on and off quickly, making it a suitable technology for storing intermittent sustainable energy in a chemical form. Nevertheless, this method suffers from an important drawback, i.e., the separation of the CO – O_2 mixture after splitting.^[7] Commonly used techniques such as centrifugation, distillation, and absorption are difficult and most certainly not energy efficient, due to the small difference in molar mass of CO and O_2 . Electrolytic membranes, which have a conductivity towards oxygen, have been proposed in literature, but they require high temperatures, again lowering the overall energy efficiency if low temperature plasmas are used.^[7] A simpler, and probably more energy-efficient way of separation is the conversion of O_2 into other molecules, which can be more easily separated from CO .

In this paper, we will demonstrate, by computer simulations and experimental validation, the in-situ chemical trapping of O_2 by the conversion of CO_2 with admixtures of H_2 or CH_4 into H_2O . This trapping of the oxygen by a chemical step is as far as we know never investigated or published, although the removal of H_2O from feedstock gases (i.e., drying) is already a widely investigated technology.^[8] As mentioned above, no energy efficient technology exists at this moment to separate the mixture of CO/CO_2 and O_2 . However, after the chemical

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trapping, a more conventional separation of the gas mixture CO/CO₂ can be performed with existing membrane technology.^[9,10] Note that this addition of CH₄ is not the same as the already existing dry reforming of methane (DRM) since in DRM it is the purpose to generate syngas (a mixture of CO and H₂), which can then be further processed by Fischer–Tropsch synthesis. In this work, on the other hand, we are looking for a way to deal with the problem of gas separation (i.e., CO, O₂, CO₂), inherent to plasma based CO₂ splitting, by trapping the atomic O into H₂O. For this reason we first investigated the effect of adding small amounts (1–5%) of H₂ to the mixture, and subsequently also CH₄, since the latter has advantages regarding cost, availability and safety over H₂. We realize that it would be even better to add green and sustainable hydrogen sources; nevertheless we first need to understand the mechanism by simple case study molecules, like H₂ and CH₄.

CO₂ splitting by plasmas is dominated by electron impact dissociation:^[11]



This reaction produces free O atoms, which will recombine to O₂. This means that the key step for the chemical trapping of O₂ is to convert the O atoms into other chemicals with a higher rate than the three-body recombination to O₂ ($k = 1.05 \times 10^{-33} \text{ cm}^6/\text{s}$ at 300 K; with any gas molecule as third body).^[11] A feasible trapping route could be the production of OH radicals through the three-body recombination of O and H atoms, which is indeed clearly faster at equal concentrations of O and H atoms (i.e., $k = 4.33 \times 10^{-32} \text{ cm}^6/\text{s}$ at 300 K).^[12]

We investigate this O₂ trapping in an atmospheric pressure dielectric barrier discharge (DBD) plasma by means of a kinetic model, supported with experiments.

1.1. Computational Method

We use a zero dimensional chemical kinetics plasma model called `global_kin`.^[13] It consists of a Boltzmann solver to obtain the electron-induced reaction rate coefficients, a chemistry module to calculate the time evolution of all species densities and an electron energy equation module to calculate the electron temperature. The chemistry model contains 62 plasma species and 520 reactions, as listed in Snoeckx et al.^[14] The full list of the neutral–neutral reactions used in the model is also presented in the supporting information. The model is applied to a DBD plasma, consisting of a large number of microdischarge filaments. The latter are accounted for in the model by assuming the power deposition to occur in consecutive triangular pulses of 60 ns with a maximum power density of $5.0 \times 10^5 \text{ W/cm}^3$. The pulse repetition frequency is 667 s^{-1} . We simulate a gas residence time of 0.74 s, i.e.,

the same as in the experiment (see Section 1.2), so this corresponds to 491 consecutive pulses. The total energy deposition is 4.2 kJ/L, like in the experiment (see Section 1.2), and results in a CO₂ conversion of $\pm 2.4\%$ when H₂ or CH₄ is added, compared to 2.7% when pure CO₂ is converted. More details about this power deposition and the model in general can be found in our previous work.^[11,15]

1.2. Description of the Experiment

The plasma reactor is a concentric DBD, as presented before,^[15] with an Al₂O₃ dielectric, a length of 9 cm and a discharge gap of 3 mm, resulting in a volume of 12.3 cm³. The total gas flow rate and electric power inserted in the plasma are kept constant at 1 000 ml/min and 100 W, which corresponds to a residence time of 0.74 s and a total energy deposition of 4.2 kJ/L, i.e., exactly the same as assumed in the model. The gas composition after plasma treatment is measured with a three-channel compact GC (Interscience), equipped with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). The first TCD channel contains a molecular sieve 5A column for the segregation of the permanent gases, while the second TCD channel is equipped with a Rt-QBOND column for the measurement of C1 and C2 hydrocarbons. The FID is equipped with a Rtx-5 column for the analysis of C1 till C10 hydrocarbons. The electrical signals are monitored by a multichannel oscilloscope (picoScope 6402A), a high voltage probe (Tektronix P6015A), and a current monitor (Pearson 4100).

2. Results and Discussion

Two different H-sources are investigated in the modelling part of this work. First, H₂ is added to CO₂, with a fraction between 0.1% and 5%. The O₂ trapping is identified by calculating the O-based selectivity of the different products as a function of the H₂ fraction.

The formulas used in the following discussion are based on the total reaction of CO₂ splitting as described in literature.^[16]



$$\text{Conversion (\%)} = \frac{\text{CO}_{2\text{inlet}} - \text{CO}_{2\text{outlet}}}{\text{CO}_{2\text{inlet}}} \times 100\% \quad (\text{E1})$$

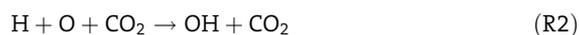
$$\begin{aligned} \text{O based CO selectivity (\%)} \\ = \frac{\text{CO}_{\text{outlet}}}{2(\text{CO}_{2\text{inlet}} - \text{CO}_{2\text{outlet}})} \times 100\% \end{aligned} \quad (\text{E2})$$

$$\begin{aligned} \text{O based O}_2 \text{ selectivity (\%)} \\ = \frac{\text{O}_{2\text{outlet}}}{\text{CO}_{2\text{inlet}} - \text{CO}_{2\text{outlet}}} \times 100\% \end{aligned} \quad (\text{E3})$$

2.1. Modelling the Oxygen Trapping Upon Addition of H₂ and CH₄

Our model predicts that in pure CO₂ only CO and O₂ are formed, with O-based selectivities of 50%, as is clear from Figure 1, but as soon as H₂ is added, the selectivity of O₂ drops significantly, and all the O₂ is replaced by H₂O at a H₂ fraction of 3%.

The mechanism behind this trapping is indeed the faster three-body recombination of O and H into OH radicals, which subsequently react further into H₂O:



Another possible H-source is CH₄, which is not only cheaper than H₂, but it also has four instead of two H-atoms available for O₂ trapping. Figure 2 demonstrates that water is again the most important trapping product, and that the O₂ is completely trapped at 2% CH₄ added to the CO₂ plasma. The maximum O-based selectivity towards H₂O is found around 1% of CH₄. A further increase in the CH₄ fraction results in the formation of methanol, which is mainly produced by:



It is also clear from Figure 2 that the CO selectivity rises above 50% upon addition of CH₄, indicating that part of the O atoms are converted into CO due to the presence of an extra carbon source (coming from CH₄ and its derivatives):

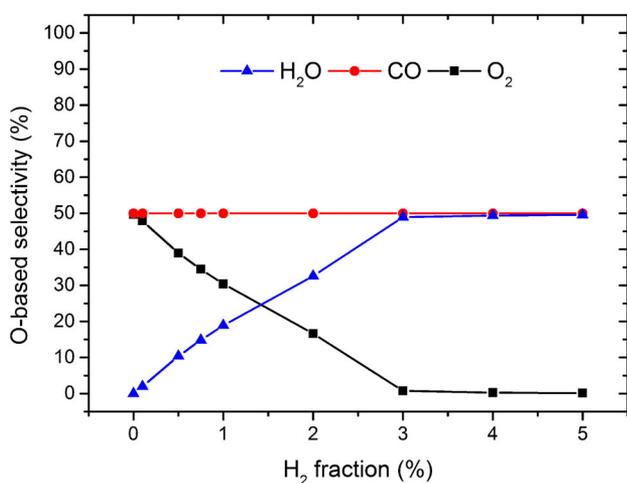


Figure 1. Calculated O-based selectivity of the reaction products as a function of H₂ fraction added to the CO₂ plasma.

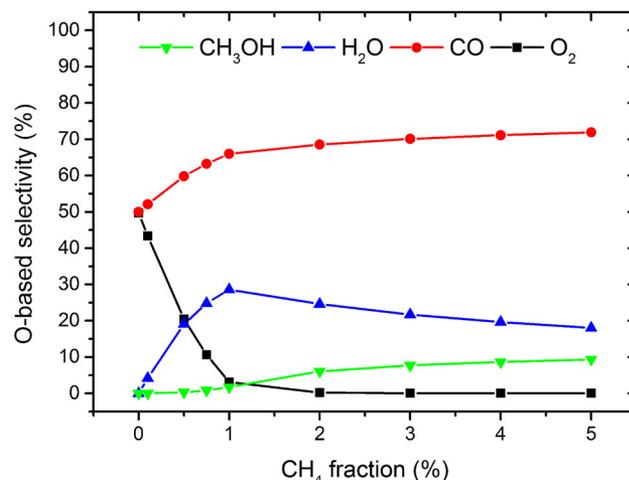


Figure 2. Calculated O-based selectivity of the reaction products, as a function of CH₄ fraction added to the CO₂ plasma.



The calculated concentrations of the gas components after plasma treatment are plotted in Figure 3, for different fractions of H₂ and CH₄ added to CO₂, as well as for pure CO₂. The remaining fraction (up to 100%) is unconverted CO₂.

It is clear that the O₂ can be completely trapped when adding 2% CH₄ or 3% H₂ at a conversion of $\pm 2.5\%$, as also demonstrated in Figure 1 and 2. Furthermore, the fraction (or yield) of CO slightly drops when adding H₂, because not all the energy put into the plasma can be used for CO₂ splitting and some energy is now also consumed by the H source.

In other words, the selectivity of CO remains 50% (see above), but the CO₂ conversion slightly drops, resulting in a somewhat lower yield of CO. In the case of CH₄ addition, however, the CO yield remains constant, because the lower CO₂ conversion is compensated by the extra C-source, yielding a CO selectivity above 50%, as explained above. Finally, we can deduce from Figure 3 that by using 3% H₂ (or more) a clean gas mixture is created with only CO, H₂O, and unconverted H₂ and CO₂. The separation of this mixture is relatively simple and/or part of it can be used directly as syngas. When CH₄ is used in small concentrations (i.e., 1%) a similar gas mixture can be reached, with only tiny fractions of O₂ and CH₄ left, but with a lower H₂/CO ratio in the syngas, as CH₄ is both a H and C source.

At higher CH₄ concentration (>2%) the O₂ is completely trapped, but a larger fraction of unconverted CH₄ remains, whereas the fractions of H₂O, H₂, and CO remain almost unchanged, so we believe that the process should be tuned in such a way that the CH₄ is completely converted, to facilitate the mixture separation.

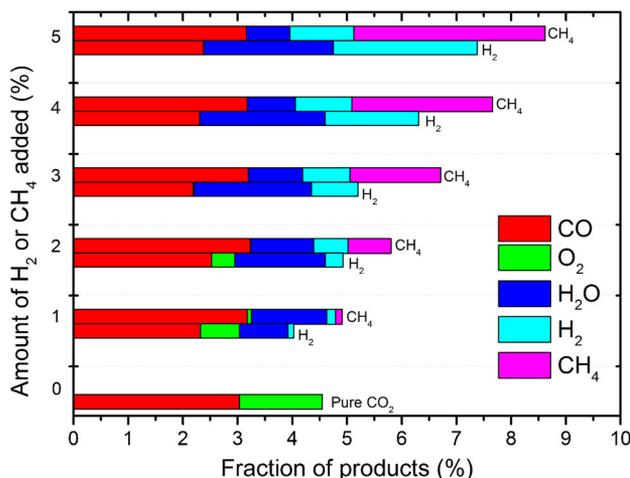


Figure 3. Calculated fractions of the various components in the gas mixture after plasma treatment, for pure CO₂ and for different fractions of H₂ and CH₄ added to the CO₂ plasma. Note that the remaining fraction (up to 100%) corresponds to unreacted CO₂.

2.2. Experimental Proof for Oxygen Trapping Upon CH₄ Addition

In order to validate these model predictions, we performed experiments for various additions of CH₄ in CO₂, for the same energy deposition and gas residence time in the plasma as in the simulations, i.e., 3.7 kJ/L and 0.74 s, and we identified the H₂O, O₂, H₂, and CO production by gas chromatography (GC). The relative concentrations (normalized to its highest area) of each component are plotted against the CH₄ fraction in Figure 4. The reason why we opted for this approach rather than a quantitative one is closely related to an inherent problem of plasma experiments. During the plasma process the gas expands (or contracts), meaning that an external calibration of the components will induce an error on the measured concentration, depending of the actual gas composition.^[17] The more classical approach to solve this problem is the use of an internal standard, but even relatively inert gases like nitrogen and argon do not behave completely inert in a plasma and will influence the conversion, which makes an internal standard not suitable for the gas mixtures under study.

Hence, considering this calibration problem, and taking into account that all the products detected by the TCD have a linear response, a non-quantitative comparison is more reliable.

Although the validation is only qualitative, a good correlation with the calculation results is found. It is indeed clear that the O₂ concentration drops significantly upon CH₄ addition, and that the trapping is almost complete at 2% CH₄, which is very similar to the model predictions in

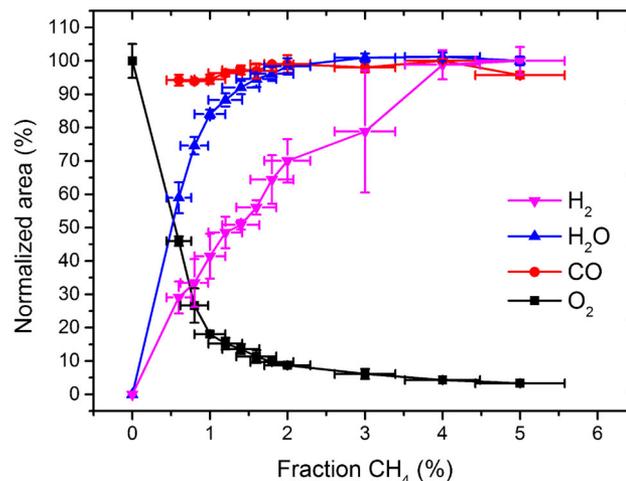


Figure 4. Measured normalized area of each product obtained by GC analysis, after plasma treatment of CO₂ with various admixtures of CH₄. Note: the 0% CH₄ point for CO is not displayed, since a split-peak method was used for the calibration of the CO and CH₄ peaks. Furthermore, we were not able to measure the CH₃OH concentration in our setup.

Figure 2 and 3. Furthermore, the production of water reaches its maximum at 2% CH₄. Further increasing the CH₄ fraction will enhance the production of different oxygenated chemicals (cf. Figure 2), which are indeed observed as trace elements in the FID, but with too low concentrations to be shown in this figure (see also below). The normalized area of CO remains almost constant upon CH₄ addition, similar to the calculation results (see reason explained above). Finally, the rising production of H₂ is also observed in the simulations (see Figure 3).

2.3. Liquids Produced: Study of the Carbon Balance Based on the Calculations

The trace elements that might be formed in the experiments where CH₄ is added as trapping agent could have an influence on the downstream processing after the chemical trapping. Although we have investigated the formation of condensing products by placing a cold trap after our reactor, not enough liquid sample could be collected to perform a proper analysis. Also heating of the tubing between the reactor and the GC did not increase the traces shown on the FID detector. However, to identify those species observed on the FID detector, a carbon balance is made based on our model calculations, and the calculated fractions of the various species are shown in Figure 5. The fractions in the carbon balance are calculated by the following equation:

$$\begin{aligned} &\text{Fractions in the carbon balance (\%)} \\ &= n \times \frac{C_n H_m O_{x\text{outlet}}}{CO_{2\text{inlet}} + CH_{4\text{inlet}}} \times 100\% \end{aligned} \quad (\text{E4})$$

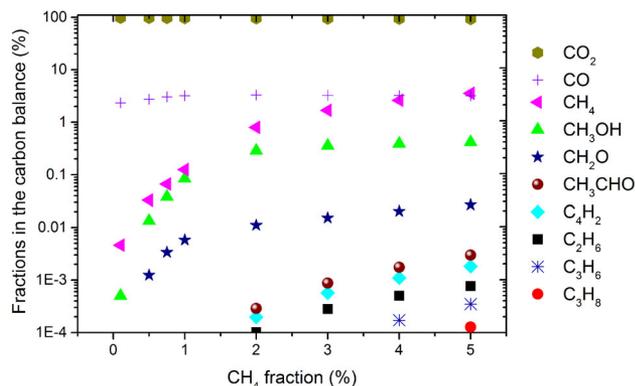


Figure 5. Calculated fractions in the carbon balance of the various components in the gas mixture after plasma treatment, as obtained from the model, for pure CO₂ and for different fractions of CH₄ added to the CO₂ plasma.

The largest fractions in the carbon balance are of course given by the unconverted CO₂, which has a fraction between 92.8% and 97.6%, and the unconverted CH₄, which fraction increases from 0.005% to 3.6% (see Figure 5). As far as the formed products are concerned, the largest fractions are given by CO and methanol. The CO fraction remains constant at about 3% upon CH₄ addition, while the methanol fraction increases with increasing CH₄ addition, until a fraction of 0.3% is reached at 2% CH₄, after which also the methanol level remains constant. The same trend can be found for formaldehyde, although its fraction in the carbon balance is more than one order of magnitude lower, with a maximum value of 0.01%. Furthermore, the addition of 2% CH₄ also gives rise to the formation of acetaldehyde with a maximum fraction of 0.003%, as well as some unsaturated hydrocarbons (such as butadiene and propene) and saturated hydrocarbons (such as ethane and propane), all with fractions below 0.001%.

The analysis of the carbon balance indicates that the production of alkanes and alkenes can be minimized as long as oxygen is available. This means that only controlled amounts of CH₄ should be added, in relation with the produced O₂, as discussed below (see Section 3).

Hence, the most likely produced liquids will be water, formaldehyde, and methanol. The latter two are quite volatile products, having boiling points below 100°C (−19.3°C for CH₂O and 64.2 for CH₃OH),^[18] making separation together with water possible. Moreover, the mixture of formaldehyde, methanol, and water is a well-known and studied mixture in the production of formaldehyde by the Formox process and could be distilled or directly used as feedstock in the process itself.^[19] Furthermore, it is stated that even in dry reforming the dominant liquid product is H₂O, with some traces of hydrocarbons, although this is highly dependent on the CH₄/CO₂ ratio.^[20]

Finally, by adding H₂, no CH_x radicals are produced, making it unlikely that hydrocarbons will be formed during the trapping process. Indeed, our calculations show that in case of H₂ addition, the highest hydrocarbon fraction in the carbon balance is formaldehyde, with a fraction below 0.001%.

2.4. Energy-Efficiency Study of the Chemical Trapping of O₂

In this section, we estimate the energy cost of the proposed method of adding either H₂ or CH₄ for O₂ trapping, compared to the energy cost of the splitting without any addition of a hydrogen source. The energy cost of producing one mole of CO by splitting CO₂ into CO and O₂ can be calculated as follows:

$$E_{\text{CO}} \left(\frac{\text{kJ}}{\text{mol}} \right) = \text{SED}_{\text{CO}_2} \left(\frac{\text{kJ}}{\text{L}} \right) \times \left[\frac{\text{molar volume} \left(\frac{\text{L}}{\text{mol}} \right) \times 100\%}{X_{\text{CO}_2} (\%)} \right] \quad (\text{E5})$$

Where SED (kJ/L) is defined as:

$$\text{SED} \left(\frac{\text{kJ}}{\text{L}} \right) = \frac{\text{Power (kW)}}{\text{Flow rate} \left(\frac{\text{L}}{\text{min}} \right)} \times 60 \left(\frac{\text{s}}{\text{min}} \right) \quad (\text{E6})$$

Note that these formulas apply both to pure CO₂ splitting and to CO₂ splitting in the case of H₂ addition. However, the formula for calculating the energy cost for producing one mole of CO in the case of adding CH₄ is slightly different:

$$E_{\text{CO}} \left(\frac{\text{kJ}}{\text{mol}} \right) = \text{molar volume} \left(\frac{\text{L}}{\text{mol}} \right) \times \left(\left(\text{SED}_{\text{CO}_2} \left(\frac{\text{kJ}}{\text{L}} \right) \times \left[\frac{1}{X_{\text{CO}_2} (\%)} \right] \right) + \left(\text{SED}_{\text{CH}_4} \left(\frac{\text{kJ}}{\text{L}} \right) \times \left[\frac{1}{X_{\text{CH}_4} (\%)} \right] \right) \right) \times 100\% \quad (\text{E7})$$

Indeed, in this case, not only CO₂ but also CH₄ can be converted into CO.

The CO₂ conversion, and the values for SED_{CO₂} and SED_{CH₄} in the case of pure CO₂ splitting, as well as when adding 3% of H₂ and 2% of CH₄ are shown in Table 1, together with the calculated energy cost for producing one mole of CO in the three cases. The small drop in SED_{CO₂} can be explained because the total SED is constant (at constant total flow rate; see equation above), but a few % is now consumed by H₂ or CH₄, respectively, so that the remaining part that can be used for CO₂ conversion is slightly lower than 100%.

The table shows that the energy cost of pure CO₂ splitting is 34.2 kJ/mol, for an SED of 4.2 kJ/L and a conversion of 2.7%

Table 1. Calculated values of CO₂ conversion, specific energy deposition for CO₂ conversion (SED_{CO₂}) and CH₄ conversion (SED_{CH₄}) as well as the energy cost for producing one mole of CO (E_{CO}) in the case of pure CO₂ splitting, as well as when adding 3% H₂ or 2% CH₄ as trapping gases.

	Conversion (%)	SED _{CO₂} (kJ/L)	SED _{CH₄} (kJ/L)	E _{CO} (kJ/mol)
Pure CO ₂ splitting	2.7	4.2	—	34.2
97% CO ₂ + 3% H ₂	2.3	4.0	—	39.9
98% CO ₂ + 2% CH ₄	2.4	4.1	0.1	37.5

(see Table 1). Adding 3% of H₂ for the complete removal of O₂ causes an increase of the energy cost by ± 6 kJ/mol. Indeed, the CO₂ conversion decreases in this case to 2.3%, which induces an increase of the energy cost to 39.9 kJ/mol. Similarly, when adding 2% of CH₄ for the complete removal of O₂, the conversion decreases to 2.4%, and this yields a total energy cost of 37.5 kJ/mol, i.e., an increase of ± 3 kJ/mol. Hence, the addition of a trapping gas (CH₄ or H₂) will lead to a small reduction of the CO₂ conversion, as a part of the plasma power will be consumed by the trapping gas. Consequently, this slightly lower CO₂ conversion results in a slightly higher energy cost for CO production.

Now we will compare this energy cost for CO production within the plasma with the energy requirements for the gas separation of the exit gas stream. Indeed, this will most probably be the most energy expensive part, and that is the reason why we propose here an alternative method, at least for the separation of O₂, which is considered to be not straightforward, as the existing membrane technology to separate CO/CO₂/O₂ is still under development.^[21,25–27] For this reason, we cannot yet put an absolute number on the energy cost for separating the CO/CO₂/O₂ gas mixture. However, we expect that this energy cost will be higher than for the separation of the CO₂/CO gas mixture, i.e., without O₂, for which technology is already available,^[9,10,22] and for which we can at least make an estimate, based on energy costs for a reference gas mixture CO₂/N₂.^[10,19] Indeed, we expect that the separation costs will be similar,^[23] or will give at least an indication. Table 2 shows the energy cost (again in kJ/mol) of different methods for separating CO₂ from a binary mixture of CO₂/N₂, together with the obtained purity of the CO₂, based on the work of Brunetti et al.^[10] It is clear that the cost of the membrane

separation technology (22–264 kJ/mol) is in the same order of magnitude, or up to a factor of 7.7 higher than the production cost of one mole of CO (i.e., 34–40 kJ/mol; cf. Table 1 above), at least in the case of a DBD reactor. Indeed, in the case of a microwave or gliding arc plasma, it can be expected that the energy cost for CO production within the plasma will be up to a factor 6 lower,^[16,24] so that the separation cost by membrane technology will be even higher in relative terms. Furthermore, the cost of absorption with monoethanolamine (MEA) and cryogenic distillation is even higher, i.e., around 176–264 and 264–440 kJ/mol, respectively (see Table 2), so this cost is clearly higher than the cost for CO production within the plasma. On the other hand, with the current membrane separation technology, the purity of the CO₂ is less compared to the absorption with MEA and especially compared to cryogenic separation (see Table 2). Hence, we can conclude that a tradeoff exists between the energy cost (which is the lowest for membrane technology) and the purity of the obtained CO₂ when separated from the CO (which is the highest for cryogenic separation).

To really estimate the effect of the chemical trapping of O₂ on the energy cost of the downstream separation, we should also compare the energy cost of separating a CO₂/CO mixture with the cost of separating a CO₂/CO/O₂ mixture. However, as mentioned above, the membrane technology for the latter separation is not yet fully developed, and therefore, it is too preliminary to put a number on this energy cost. Currently, this technology operates at temperatures above 700 °C,^[21,25–27] so we expect that the energy cost will be higher than for separating the CO₂/CO mixture by membrane technology, where the operation temperature is close to room temperature. Furthermore, to our

Table 2. Energy cost of different CO₂ separation systems, as well as the obtained CO₂ purity.^[10]

	Membrane technology	Absorption with MEA	Cryogenic separation
Energy cost (kJ/mol)	22–264	176–264	264–440
CO ₂ purity (%)	80–95	>95	99.99

knowledge, the only commercially existing technology at this moment to separate a CO/CO/O₂ mixture with a high purity is cryogenic separation,^[10] which typically has higher energy costs than membrane technology (see Table 2). Hence, we expect that the energy cost for separating the CO₂/CO/O₂ mixture will be certainly higher than for separating the CO₂/CO mixture, which is already higher than (or in the best case comparable to) the energy cost of producing one mole of CO within the plasma, even when adding a trapping gas (cf. Table 1 and 2 above). Therefore, based on these estimates and considerations, we expect that this chemical method of O₂ trapping will be an energy efficient alternative to gas separation methods.

3. Conclusion

To conclude, we demonstrated by a combination of modelling and experiments the possibility to chemically trap O₂ during the plasma splitting of CO₂ by the addition of H₂ or CH₄. The addition of a few % of either H₂ or CH₄ seems enough to trap the O₂ completely, and produce H₂O instead. We should, however, point out that in our case, the CO₂ conversion was only a few %, and at higher conversion also more H₂/CH₄ would be needed to trap the O₂. However, to prevent that dry reforming occurs at high conversions, resulting in the formation of hydrocarbons, the addition of CH₄ should be controlled as a function of the residence time, so that the kinetics favor water production instead of dry reforming. The concept of adding a small amount of reactants is already proven in the production of fine chemicals by plasma, favoring the production of one type of molecule.^[28] One possible way to accomplish this is by using a recycle stream, in such a way that the outlet stream is dried (H₂O is removed) and the CO₂/CO mixture is separated, so that the separated non-converted CO₂ can be re-mixed with a fresh inlet stream containing a hydrogen source. A second possibility would be to use a couple of DBD reactors in series, in such a way that after each reactor the gas is dried (H₂O is removed), leaving only CO and CO₂ as outlet stream. A small amount of hydrogen source could then be added before each individual reactor, and at the end of the reactor series a gas will be produced without O₂ and with a high conversion towards CO.

In the case of CH₄ addition, also H₂ is formed. If we compare the two admixtures, CH₄ is probably the better choice since it requires smaller fractions for O₂ trapping, and it is less expensive compared to H₂. We should point out that the purpose of this research was to identify a chemical removal mechanism by OH radicals. Although we only investigated H₂ and CH₄, in principle, more green and sustainable sources for OH or H could also be used (for example, glycerol)^[29] to make this approach probably more interesting and cost efficient. Moreover Tagawa et al.^[30]

showed that by removing O₂ from the plasma, the CO₂ conversion increased up to 40%. Hence, their results obtained with a hybrid reactor existing of a Solid Oxide Electrolyser Cell and a DBD indicate that separation of O₂ not only solves a downstream problem (further processing) but gives also rise to a higher conversion.

To conclude, it is clear that the trapping of O₂ during the CO₂ splitting can be accomplished by a simply chemical step, making the separation of end-products possible with the existing membrane technology for CO₂ separation.

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