

Post-plasma carbon bed design for CO₂ conversion: Does size and insulation matter?

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ABSTRACT

We present the performance of a post-plasma carbon bed for improving plasma-based CO₂ conversion, studying the effect of bed length and additional thermal bed insulation. The experiments were conducted using an atmospheric pressure gliding arc plasmatron in both high and low specific energy input (SEI) regimes. Each bed was equipped with a silo to enable continuous carbon feeding and operation for an order of 1 hour, thus overcoming previous limitations in literature. Importantly, we derive an improved energy efficiency (EE) calculation with an accurate and unambiguous consideration of the key reaction contributions of both plasma and carbon bed. This derivation serves to highlight the inconsistencies that arise in determining EE in such a complex chemical system. We therefore advise and advocate for the use of energy cost (EC) as the key reported energy metric in systems using post-plasma carbon beds. The optimum conversion and energy metrics were obtained with the longest bed, reaching a conversion of 41 %, an EE of 51 % and an EC of 0.41 MJ/mol at high SEI. The design of the insulated bed and silo allow for previously unreported preheating of the carbon, which reduces oscillations observed in the conversion profiles of the short and long beds. Preheating of the external silo for the long bed also yields a near-complete removal of oscillations. Finally, when comparing our performance with results from literature for post-plasma carbon beds, our system clearly improves upon the state-of-the-art, both in absolute values of conversion and

energy metrics at the same SEI, as well as by sustaining this improvement for extended periods of time.

Keywords: Carbon bed, Reverse Boudouard reaction, Warm plasma, CO₂ conversion

1. Introduction

Carbon capture and utilisation (CCU) is growing in importance to mitigate anthropogenic emission of carbon dioxide (CO₂) into the atmosphere. Utilisation methods aim to convert the captured CO₂ into more useful chemical building blocks such as carbon monoxide (CO). Competing technologies under investigation in the field include thermocatalysis [1,2], electrocatalysis [3,4], photocatalysis [5,6] and plasma [7-9]. Plasma-based solutions offer a flexible option, that can quickly be switched on/off, compatible with a variable renewable energy supply and typically with a relatively small footprint. Different types of plasma have been investigated in this regard, with varying degrees of non-equilibrium between gas and electron temperatures [8]. Cold plasma devices such as dielectric barrier discharges (DBDs) exhibit a high degree of said non-equilibrium, with gas temperatures close to ambient and electron temperatures around two orders of magnitude greater. Such devices typically result in relatively high conversion (up to 40 %), albeit at low energy efficiency (EE) (at maximum ca. 10 %) [8,9]. Quasi-thermal, or “warm”, plasma reactors have also been studied extensively, wherein the degree of non-equilibrium is much lower, and the gas temperature is often in the order of several thousand Kelvin. These setups are typically limited by the fraction of gas treated by the plasma and the rapid recombination of CO and O/O₂ into CO₂, resulting in lower conversions (10 – 12 %) but higher EE (30 – 40 %) than cold plasma discharges [8-10]. Basic reactor modifications (e.g. internal flow pattern variations [10]/electrode geometry [11]) fail to

breach the EE target of 60 % cited as the goal for plasma-based CO₂ conversion technology [7,8].

As mentioned above, the main factor hindering the process development is the recombination reaction of CO with O and/or O₂ (both formed from CO₂ plasmolysis) back into CO₂. Several post-plasma modifications have been investigated as directions to tackle this problem. Converging nozzles that constrict the post-discharge gas stream have shown promise when applied to warm plasmas [12,13]. Hecimovic *et. al* showed that a post-plasma nozzle improved the mixing of the cold insulating swirling gas with the high temperature gas from the discharge region, effectively quenching the gas temperature and reducing the recombination reaction [12]. Their nozzle was also water-cooled, allowing for further conductive heat dissipation through the walls. In their most recent work with an atmospheric pressure microwave (MW) plasma and a multi-channel water-cooled nozzle [14], they achieved a near five-fold conversion improvement (from 12 % to 57 %) at a specific energy input (SEI) of 7 eV/molecule. A clear disadvantage of water-cooled nozzles is the conductive heat-loss to the water-cooled nozzle walls, which requires heat-recovery systems to reduce the energy loss from the system. Furthermore, as the nozzle does not remove the O₂ produced, the addition of a nozzle does not inherently solve the problem that plasma-based CO₂ conversion results in a three-component mixture (CO₂/CO/O₂), which will result in further separation costs downstream in an industrialised setting.

Another promising direction for enhancing CO₂ conversion performance in warm plasmas is the removal of the formed O₂ via absorbing membranes inserted into the effluent stream. Antunes *et al.* recently demonstrated this proof of concept using perovskite membranes downstream in an atmospheric pressure MW discharge [15]. Under their best conditions, they managed to remove ca. 5 % of the produced O₂ from the effluent stream. The technology shows

potential but is currently operated with an inert gas (argon in this study), which will incur further costs upon scaling up.

An alternative post-plasma modification with the same goal of removing O₂ from the effluent is the implementation of a carbon bed, wherein a solid carbonaceous material is added into a reaction chamber close to the discharge. This material, often derived from other waste streams [16,17], can react with the effluent species, potentially boosting conversion while simultaneously removing O₂ and increasing the output concentration of the desired product CO (see Eqs. 1-3). The main reactions between gaseous species and solid carbon involved in this process are [18]:



With the addition of reactants such as solid carbon to a system, the inherent complexity increases and several reactions may proceed concurrently, such as CO₂ dissociation and the reverse Boudouard reaction (RBR, Eq. 3).

To the best of our knowledge, there are no publications to date which collate all current works on the topic. Hence, in Section 2 we first present a detailed overview of current works on this topic. After describing the experimental setup (Section 3), we then derive more accurate equations for the calculation of EE, including the relative pertinent reaction contributions and their assumptions, in Section 4. Therein, we also highlight the fact that the calculation of EC is more straightforward and requires fewer assumptions. In Section 5, we present our results and discuss in detail the varied performances of the three carbon bed designs. Additionally, we collate the literature works with their best performance metrics (CO₂ conversion, EE and energy cost (EC)) summarized, together with our best results in this section.

2. Literature overview of plasma-based CO₂ conversion with a post-plasma carbon bed

One of the first reported cases of such a method applied to a plasma system was by Uhm *et al* [19], wherein the authors introduced a coal powder downstream from their CO₂ MW discharge. In this work, they initially characterised the effluent of the CO₂ discharge in the absence of the coal powders using optical emission spectroscopy (OES) to determine the rotational temperature (T_r) of hydroxyl radicals obtained from the dissociation of a miniscule fraction of H₂O molecules added to the inlet stream (1 vol%). This rotational temperature was assumed to be equal to the heavy particle temperature (T_g) due to fast rotational-translational relaxation that occurs at atmospheric pressure. The gas temperature ranged from 6700 K closest to the discharge decreasing to 2550 K at 9 cm downstream. When introducing the coal powders, they achieved an optimum conversion of 40 % at their highest SEI condition (24 kJ/L, 5.99 eV/molecule, i.e., high power of 4 kW and low flow rate of 10 L/min).

Liu *et al.* [20] utilised an atmospheric pressure thermal plasma torch operated in Ar and CO₂ to react with coke particles of 5 – 8 mm in diameter. In terms of conversion, their best result (95 % conversion) was obtained using an applied power of 16 kW to a discharge composed of a near 1:1 mixture of Ar and CO₂ (25 L/min and 26 L/min, respectively). Increasing the CO₂ fraction to a maximum of 1:1.4 (Ar:CO₂) at a fixed applied power (14 kW) resulted in a lower conversion of 68 %, albeit with an improved EE of 82 % and EC of 0.34 MJ/mol CO. It should be noted that this EE value is most likely slightly overestimated due to the competing reactions of pure CO₂ dissociation and the reverse Boudouard reaction (RBR), with the latter having a lower standard reaction enthalpy. As mentioned in Section 1, the over- or underestimation of EE is commonplace in post-plasma carbon bed literature due to these competing reactions. Therefore, we outline a new calculation in this work to account for this, as given in Section 4 (Metrics calculation and analysis).

Li *et al.* [21] followed up the work on this setup, investigating the influence of injecting the CO₂ into the afterglow of the thermal plasma discharge (as opposed to using it as one of the discharge gases), and they also performed OES on the afterglow to determine the constituent species. When CO₂ was injected into the afterglow of an Ar/N₂ discharge, no C₂ Swan band emission was detected, indicating a lack of CO₂ dissociation. In the case when CO₂ was used as a discharge gas, the inlet stream was diluted with Ar, similar to the work of Liu *et al.* [20]. Under these experimental conditions, C₂ Swan band emission was observed in the afterglow (indicative of CO₂ dissociation) and the CO₂ conversion doubled from 35 to 70 %. The authors attributed this increase to the combination of plasma-based CO₂ dissociation and RBR in the carbon bed. It should be noted however that the use of Ar as a co-reactant will incur further costs and require additional separation stages downstream to isolate the CO produced.

Huang *et al.* [22] demonstrated the first implementation of a post-plasma carbon bed with a gliding arc (GA) plasma reactor. The authors initially characterised their rotating GA in the absence of carbon, capturing the ignition, elongation, extinguishing and re-ignition cycle typical to GA discharges using a high-speed camera and voltage/current probes. The frequency of this cycle rose while the plasma length shortened as a function of increasing flow rate, due to the amplified convective heat transport at the higher flow rate. In the presence of carbon, the peak CO₂ conversion improved from ca. 7 % to 21 %, however at the expense of EE, which lowered from 36 % to 24 %. The observed reduction in EE occurs because the optimum flow rate for conversion when biochar is present is lower than in the empty reactor case. The authors attributed this peak shift to the mesh covering of the outlet of the reactor, which visually decreased the afterglow volume.

Zhang *et al.* [23] investigated the use of a warm plasmatron reactor operated in pure CO₂ in combination with a carbon bed. They compared the efficiency of a fixed and fluidized carbon bed, in addition to researching the implemented biochar properties. Upon comparison of the

beds, they observed that the fixed bed performed better in terms of conversion and EE under almost all flow rates investigated. As similar SEI values (hence relatively equal plasma-based power at a fixed flow rate) were recorded at each flow condition, they attributed the difference to a combination of a lower measured gas temperature and a higher recombination rate for the produced CO and O₂ due to a longer pathway prior to reacting with the biochar in the fluidised bed. In terms of biochar properties, the main factor identified by the authors was the carbon content – materials with higher carbon content (determined by elemental analysis) performed the best. Interestingly, when comparing a single biochar source pyrolyzed at three different temperatures, the results indicated both that a higher carbon content was beneficial, but also that increasing the surface area of the material by an order of magnitude did not affect the performance to a similar level.

A previous work from our group conducted by Girard-Sahun *et al.* [18] implemented a combined experimental and modelling approach to provide more insight into their results. In addition to this two-pronged approach, they also developed a silo system to enable continuous carbon feeding and replenishment of the bed throughout the course of an experiment. The experiments were carried out using a gliding arc plasmatron (GAP) reactor and an AC power supply to reduce electrode degradation. Upon ignition in the presence of carbon, the authors recorded peaks of CO production and CO₂ destruction, reaching a conversion up to 13 %. However, after a few minutes this value dropped to around 5 %, lower than the steady-state value of 8 % obtained in the absence of carbon. This reduced performance indicates that the silo system was not working efficiently. Their quasi-1D model suggested that this transient behaviour in the presence of carbon was due to the oxidation of the surface of the carbon particles. Initially, this produces CO *via* the RBR, but subsequent coverage of oxygen complexes favours the production of CO₂ instead [18], which resulted in a lower conversion than the benchmark case. The authors suggest this oxygen coverage can be limited by providing

a higher bed temperature, either through additional heating or by supplying more power to the system, but such experiments were not carried out in their study..

Most recently, Wu *et al.* [24] coupled an atmospheric pressure MW plasma to a carbon bed, utilising Ar and CO₂ as input gases. They initially characterised the afterglow using OES, observing a higher intensity of C₂ Swan band emission with increasing power due to improved CO₂ dissociation in the larger plasma volume. Interestingly, they also spatially defined the axial lifetime of C₂ and atomic O species, demonstrating a near-complete removal of both ca. 3 cm downstream from the mounting hole of their waveguide. Upon introducing biochar to a fixed carbon bed downstream, the authors first tested the effect of the Ar dilution on its performance, observing a near-linear rise in absolute CO₂ conversion with increasing fraction of Ar. The EE peaked at 30-40 % Ar and decreased at higher fractions owing to the imbalance of energy supplied to Ar ionisation and CO₂ dissociation. Finally, they tested char from two different sources (coconut shell and bamboo), achieving an optimum absolute CO₂ conversion of 75 % for a corresponding EE of 30 % with the smaller coconut shell char. However, the effective CO₂ conversion, accounting for the fraction of CO₂ in relation to the total feed gas mixture (see further), was 60 %.

It is clear that previous works on the topic have extensively investigated the effect of (i) process parameters (temperature, SEI), (ii) the nature and type of carbon materials, and (iii) the nature of carbon bed (fixed or fluidized) for this process. To date, however, the insights into the best design of fixed carbon beds are clearly lacking. In this work, we focus on the reactor setup and effect of carbon bed design on the efficiency of the process, namely the effects of bed length and additional bed insulation. To this end, we tested three different carbon beds with the same type of activated carbon at two distinct SEI values in a GAP reactor, and we demonstrate the optimum functioning of the silo system. The effect of additional pre-heating of the external silo, also to overcome the limitations encountered by Girard-Sahun *et al.* [18] was also

investigated. In addition, we present an updated method for calculating the EE of the process, based on the work of Zhang *et al.* [23], clearly elucidating the contribution of direct CO₂ dissociation from the plasma and of the RBR at the carbon bed to the EE of the process using simple process outputs.

3. Experimental

The experiments carried out in this work were conducted using a gliding arc plasmatron (GAP) developed by Nunnally *et al.* [25] and used in previous works within our group [10,11], including with a post-plasma carbon bed [18]. A basic schematic of the reactor setup configured with an external silo is outlined in Fig. 1a. While the same reactor was used, there were some notable differences to the setup used in previous works within our group. The material of the electrode insulation pieces was changed from Teflon to ceramic (top piece Macor, bottom piece alumina) to enable longer operation times and higher currents to flow through the reactor. This is important to realize a higher carbon bed temperature, and thus for improving the effect of the carbon bed. A detailed schematic of the cathode and anode housing, including the ceramic insulation piece, is shown in Fig. 1b. To increase the contribution of the endothermic RBR, the power supply unit (PSU) was also changed from AC to DC (Technix, SR12KV-10KW) to increase the gas temperature of the effluent [26].

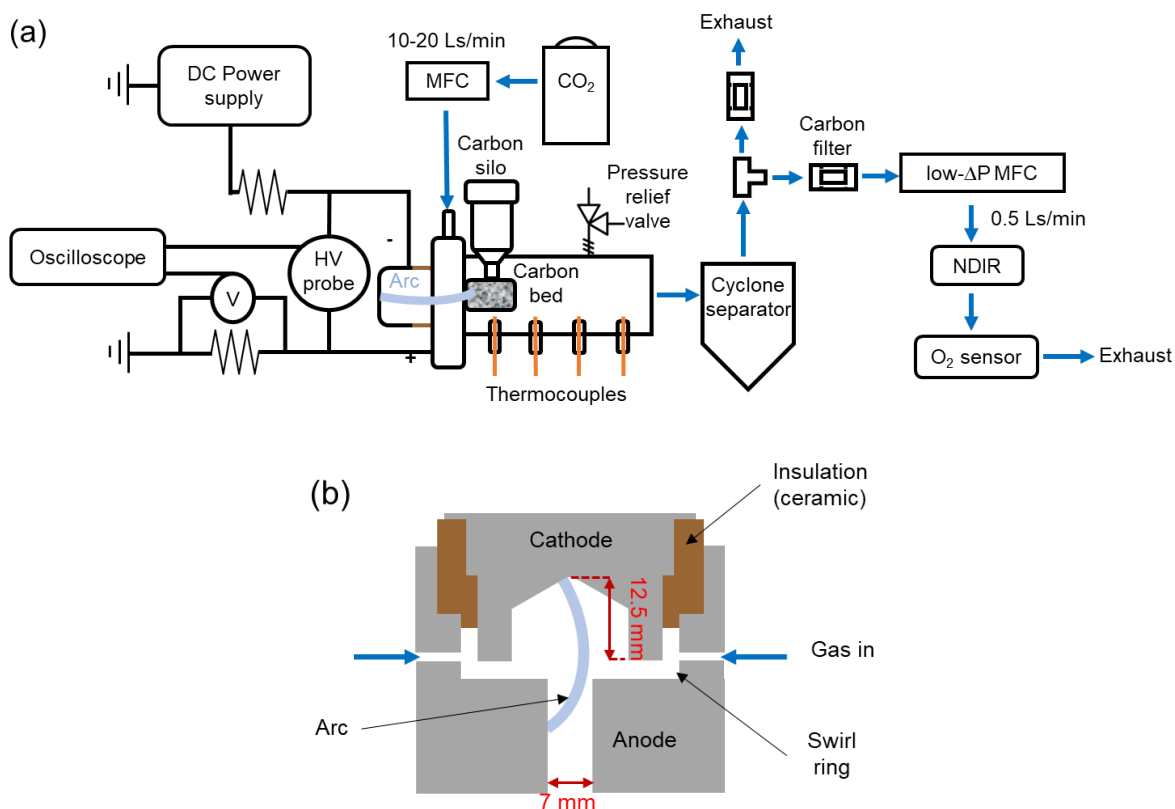


Fig. 1. Representative (a) reactor setup schematic shown for a configuration utilising external silo and (b) detailed cathode/anode coupling showing insulation and swirl ring (with six tangential gas inlets).

Pure CO₂ (99.999 %, Air Liquide) was supplied to a single gas inlet connected to a swirl ring containing six tangential inlets, and the flow rate was controlled using a mass flow controller (MFC) (Bronkhorst, F-201A). The outlet mixture was analysed using non-dispersive infrared (NDIR) detectors for CO and CO₂ (SmartGas, FLOW-EVO) and an optical sensor for O₂ (Pyroscience, FDO2). A small-scale cyclone separator and in-line filters were installed between the reactor and analytics/exhaust to remove solid dust particles and prevent contamination of the sensors (see Fig. 1a).

The negative polarity current-controlled source was connected to the high-voltage electrode while the reactor body was grounded. The voltage was initially set to 12 kV to initiate the gas breakdown at the shortest distance, while the working voltage was free to vary according to the

plasma length and resistivity (typically 1 – 1.5 kV). The voltage differential across the plasma was measured using a high-voltage probe (Tektronix, P6015A) connected to the cathode and ground connection. The current was measured using a current sense resistor (2 ohm) connected to a digital oscilloscope (Keysight, DSOX1102A) in addition to the high-voltage probe. A ballast resistor (200 ohm) was placed in series between the PSU and reactor to increase the resistive load detected by the PSU, resulting in a more stable discharge. The plasma typically exists in a takeover mode [27,28], manifested as quasi-periodic peaks in current and voltage. An example oscillogram demonstrating these fluctuations in voltage and current is shown in the Supporting Information (SI, Fig. S1). A high SEI value around 6.8 kJ/L (1.7 eV/molecule) and a low SEI value around 3.7 kJ/L (0.92 eV/molecule) were applied to each of the different bed configurations.

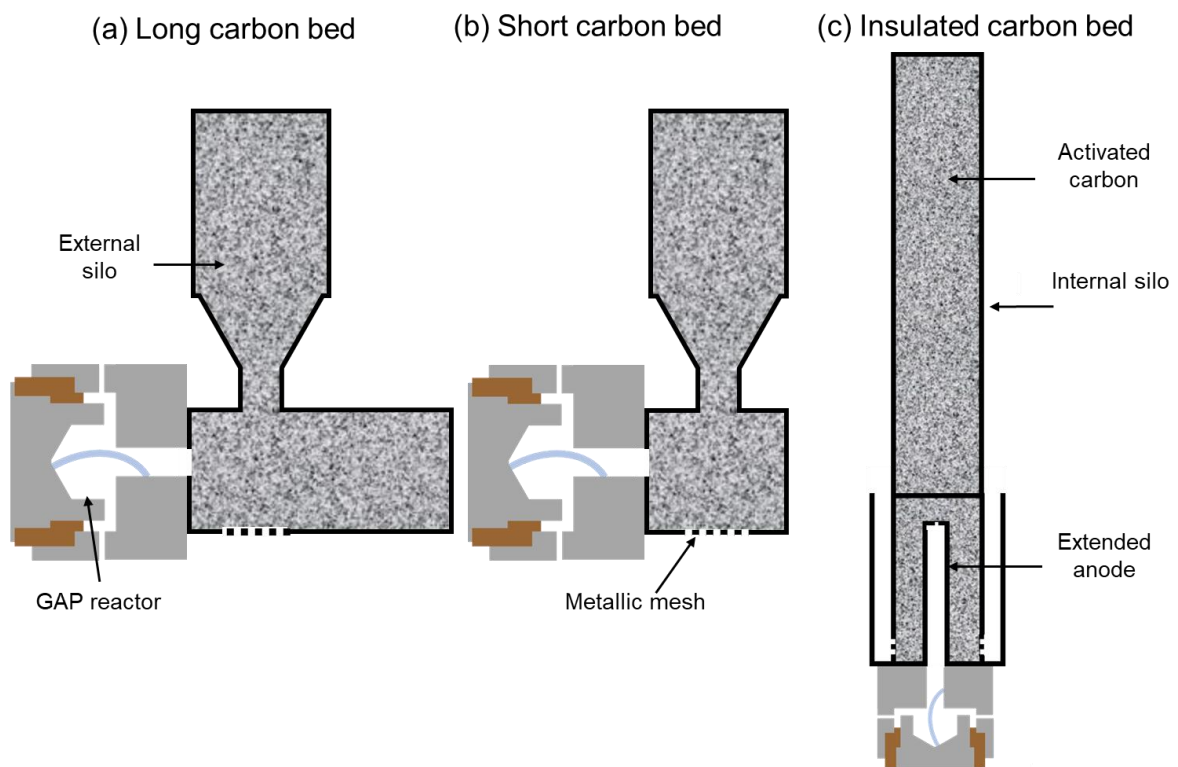


Fig. 2. Illustration of (a) long, (b) short and (c) insulated carbon beds with coupled silos.

In each experiment, 80 g of steam-activated carbon pellets (Norit ROW, 0.8 mm diameter) were loaded into the silo and bed. The 'long bed' outlined in Fig. 2(b) is the same as used by Girard-Sahun et al. and was coupled to the previously developed silo system, but now properly functioning (see below, Sections 5.1.1 and 5.5). The 'short bed' (Fig. 2b) has an identical design and diameter as the long bed, differing only in the length, which was approximately halved (long bed = 35 mm, short bed = 15 mm), with the purpose of heating a smaller volume of carbon to an adequate temperature to facilitate the RBR. This bed was operated with the same external silo as the long bed. The third design ('insulated bed', Fig. 2c) differs from the previous two as it contains an elongated anode tube and an additional layer. The elongated anode tube was implemented to reduce arc disruption of fresh carbon flowing from the silo into the bed and the extra layer requires the hot effluent gas to pass through the carbon bed and back around it, creating an insulating layer of high-temperature gas. The additional layer was implemented to maintain and, more importantly, to increase the average bed temperature, an effect that was highlighted by our previous modelling study as key to improving carbon bed performance [18].

The temperature along the length of the reactor was monitored using a digital thermometer (Omega, HH520) with thermocouples (K-type) inserted into the exhaust chamber at four locations (see Fig. 1a). Direct measurement of the temperature inside the beds was not possible as the temperature within the beds was above the limit of K-type thermocouples ($>1260\text{ }^{\circ}\text{C}$).

To test the effect of pre-heating the external silo coupled to the short and long beds, a heating tape (Isopad, TD7000) was wrapped around the filled stainless steel silo (see SI, Fig. S2). This line was heated to a temperature of $150\text{ }^{\circ}\text{C}$ and maintained at this value for at least 4 hours. Once this pre-heating time had elapsed, the experiment was started with the heating tape remaining in place.

4. Metrics calculation and analysis

Our group previously emphasized the importance of uniform and precise methods for calculating process metrics, including those for CO₂ plasmolysis [29]. Here, we calculated the conversion, SEI and EC according to formulae derived therein. To accurately calculate the conversion, the volumetric flow rate at the outlet (Q_{out}) is required. In this work, we utilise the oxygen balance to determine Q_{out} in the same manner as Zhang et al. [23]. In their work, they compared the calculated flow rate to the measured one using a volumetric flow meter and observed good agreement for their experimental conditions. As such, Q_{out} (L/min) was calculated by:

$$Q_{out} = \frac{2 * Q_{in}}{(2 * (\gamma_{CO_2} + \gamma_{O_2}) + \gamma_{CO})} \quad (4)$$

Where Q_{in} is the volumetric flow rate at the inlet (L/min) and γ is the fraction of the component indicated in the subscript (i.e. CO₂, O₂ or CO). Using this definition, the conversion (X , %) is calculated according to:

$$X = \frac{Q_{in} - (Q_{out} * \gamma_{CO_2})}{Q_{in}} * 100 \quad (5)$$

Wherein 100 is the conversion from fraction to percentage (%). The SEI (kJ/L) is the ratio of power to flow rate, defined as:

$$SEI = \frac{P}{Q_{in}} * 60 \quad (6)$$

In this equation, 60 is the number of seconds per minute (s/min) and P is defined as the plasma-deposited power (kW) which does not account for power losses incurred from the power supply or the ballast resistor. While we acknowledge the importance of reporting the plug power to assess the industrial viability of plasma processes [30], in this work we focus on the plasma

power to enable direct comparison to other works in literature, which almost exclusively report plasma power. The units of SEI can be set as kJ/L, kJ/mol and eV/molecule, the conversions for which are shown in Eq. 7 and 8. .

$$\text{SEI [kJ/mol]} = \text{SEI [kJ/L]} * V_m \quad (7)$$

$$\text{SEI [eV/molecule]} = \text{SEI [kJ/mol]} * \frac{6.242 \times 10^{21}}{N_A} \quad (8)$$

Where V_m is the standard molar volume (24.06 L/mol at 293 K and 1 atm, i.e. standard EU = normal USA [29]), 6.242×10^{21} is the amount of electron volts per kilojoule (eV/kJ) and N_A is Avogadro's constant (6.022×10^{23} molecule/mol). It should be noted that careful consideration should be given to the value elected for V_m , as this varies depending on the definition of reference temperature and pressure.

As mentioned in the Introduction, several previous works have attempted to define the EE when utilising a post-plasma carbon bed for improving CO₂ conversion. Since two reactions of CO₂ conversion take place, this metric requires the use of two standard reaction enthalpies (ΔH_r°), namely that of CO₂ dissociation ($\Delta H_r^\circ = 283$ kJ/mol) and of the RBR ($\Delta H_r^\circ = 172.5$ kJ/mol).

Huang et al. [22] and Zhang et al. [23] derived contribution equations for each reaction based on the oxygen balance (see SI, Section S2). However, problems arise within these formulae when the detected O₂ fraction at the outlet becomes zero (as is the case in our work and most other post-plasma carbon bed works). In this scenario, the contribution of the plasma-based dissociation becomes zero, meaning the RBR becomes responsible for the entirety of the CO₂ conversion obtained. Since the enthalpy of the RBR is lower than that of CO₂ dissociation, this leads to an underestimation of the EE.

In reality, a significant part of the measured CO₂ conversion is due to the initial plasma-based dissociation, which cannot be captured by the formulae derived by Huang and Zhang *et al.*. Hence, we propose an alternative set of equations, based on the results obtained using an empty bed at the same SEI as recorded in a corresponding filled bed experiment. By using these values, the relative contributions can be calculated as follows:

$$\alpha_{\text{Dissociation}} = \frac{X_{\text{empty}}}{X} \quad (9)$$

$$\alpha_{\text{RBR}} = 1 - \alpha_{\text{Dissociation}} \quad (10)$$

Where α is the unitless contribution factor (between 0 and 1), with the subscript defining the pertinent reaction, X_{empty} is the conversion obtained in an empty bed (%) and X is the conversion obtained in the presence of carbon (%). These equations require two key assumptions, namely:

1. The overall conversion of CO₂ based on plasma-based dissociation is constant in the presence and absence of carbon.
2. The reaction of produced O₂ with carbon results in only the formation of CO and not CO₂.

We tested the first assumption by packing an inert material (Al₂O₃ spheres) into the insulated bed and comparing the conversion to the empty bed result. The deviation between the inert packed and empty insulated bed conversions was small enough (8.8 % and 8.2 %, respectively) to consider this assumption valid. The same test could not be conducted in either the short or long bed as the plasma afterglow is in direct contact with the material in these configurations, resulting in damage and decomposition of the materials. The second assumption appears to be valid provided the CO₂ concentration detected does not exceed that detected during the empty bed experiments. If the opposite is assumed (i.e. formed O₂ reacts with solid carbon to form

CO₂), the conversion would remain the same, but the EE would deviate slightly, as illustrated in the numerical example in SI (Section S3).

Thus, the equation for the EE (%) defined by Huang et al. [22] and Zhang et al. [23] can be utilised with these new definitions for the contributions:

$$EE = \frac{X * (\alpha_{\text{Dissociation}} * \Delta H_{r,\text{Dissociation}}^{\circ} + \alpha_{\text{RBR}} * \Delta H_{r,\text{RBR}}^{\circ})}{SEI} \quad (11)$$

Where $\Delta H_{r,\text{Dissociation}}^{\circ}$ is the standard reaction enthalpy for CO₂ dissociation (283 kJ/mol), $\Delta H_{r,\text{RBR}}^{\circ}$ is the standard reaction enthalpy for the RBR (172.5 kJ/mol), α is the contribution factor with the subscript defining the pertinent reaction and SEI is defined in kJ/mol.

Another, more simplified process efficiency metric is the EC (MJ/mol). This parameter combines the conversion and SEI parameters into a quantifiable measure of the energy expenditure of the process. In situations where determining the pertinent reaction pathways and their relative contributions to EE can be difficult, EC is a more useful metric as it provides a simple number without the need for assumptions or detailed reaction pathway analyses. It is defined as:

$$EC = \frac{SEI * V_m}{X/100} * \frac{1}{1000} \quad (12)$$

In this equation, the denominator 100 (%) is to retrieve the conversion as a fraction and 1/1000 is the ratio of MJ to kJ (MJ/kJ). As X is the percentage conversion of CO₂ (%), the EC is technically represented as MJ/mol CO₂. For simplicity, we will refer to the unit of EC hereafter as MJ/mol. To convert the units of EC from MJ/mol to eV/molecule, the following formula can be used:

$$EC \text{ [eV/molecule]} = EC \text{ [MJ/mol]} * \frac{6.242 \times 10^{24}}{N_A} \quad (13)$$

Where 6.242×10^{24} is the amount of electron volts per megajoule (eV/MJ). In the presence of carbon, the concentration of O₂ remained negligible (<0.1 vol%) in each experiment. Once the carbon is fully consumed, the O₂ concentration rises (see SI, Fig. S3) marking the time point after which the experiment was concluded. In addition to this, the CO and CO₂ profiles were temporally stochastic in nature, especially with the short and long bed configurations. Such profiles make the calculation of conversion more difficult than steady-state systems. The volumetric outflow (Q_{out}) and conversion profiles for each repeat were calculated directly using these oscillating profiles, with an average conversion value determined from three of these oscillating conversion profiles during the pseudo-steady state that appeared after some duration. An example of the oscillating concentration and conversion profiles is also shown in SI (Fig. S3), with the latter highlighting the pseudo-steady state region.

Due to these oscillations, the standard deviation of these metrics appears large when plotted in the following figures. For the EE and EC, the error was propagated using the standard deviations and partial derivatives (with respect to their variables) of the conversion and SEI values.

5. Results & discussion

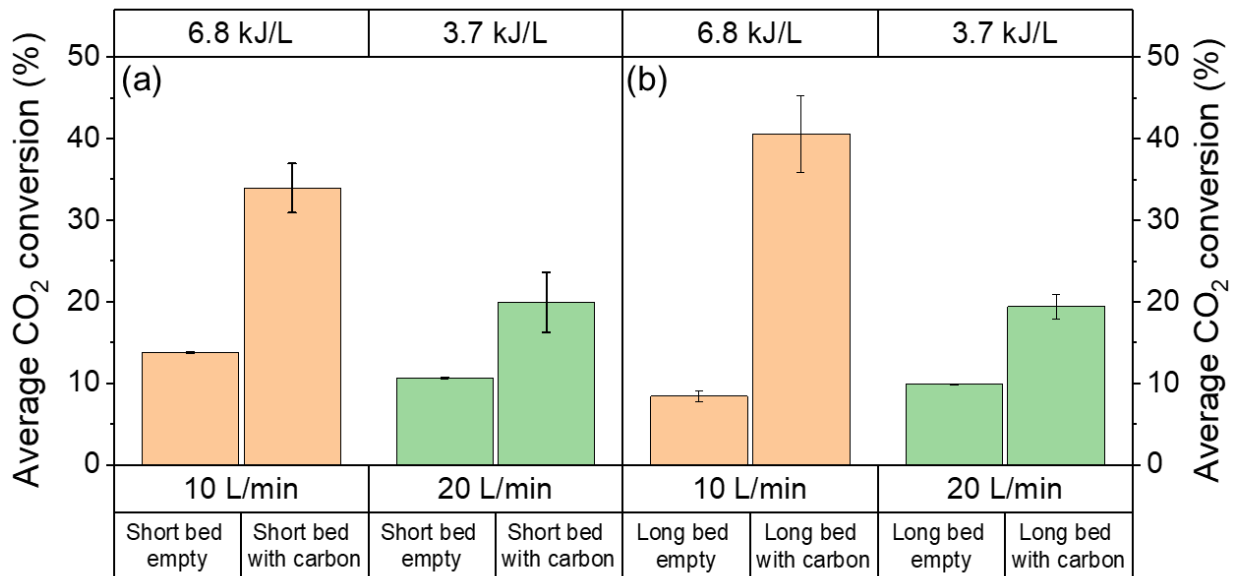
For each stage in this investigation, we examined and compared the effect of two different SEI values (i.e. ratio of power to flow rate) on the conversion and energy metric performances. In each case, the flow rate was fixed and the SEI values between the beds were aligned by varying the power delivered by the PSU. For this purpose, the current was adjusted and the voltage was allowed to vary in response to the resistivity of the system. For the high and low SEI conditions, the flow rate was set to 10 L/min and 20 L/min, respectively, resulting in SEI values around

6.8 kJ/L (1.7 eV/molecule) and 3.7 kJ/L (0.92 eV/molecule). During each experiment, less than 0.1 % of O₂ was detected in the effluent stream for the duration of the experiment when carbonaceous material was present in the bed. This means the carbon bed was always effective for removing the O₂ produced by CO₂ splitting, which will lower the overall separation costs of plasma-based CO₂ splitting.

5.1. Effect of bed length

5.1.1. Conversion and concentration profiles

We investigated the effect of bed length by comparing the average CO₂ conversion obtained with the short and long beds in Fig. 3(a) and Fig. 3(b), while the CO and O₂ concentrations for these conditions can be seen in Fig. 3(c) and Fig. 3(d).



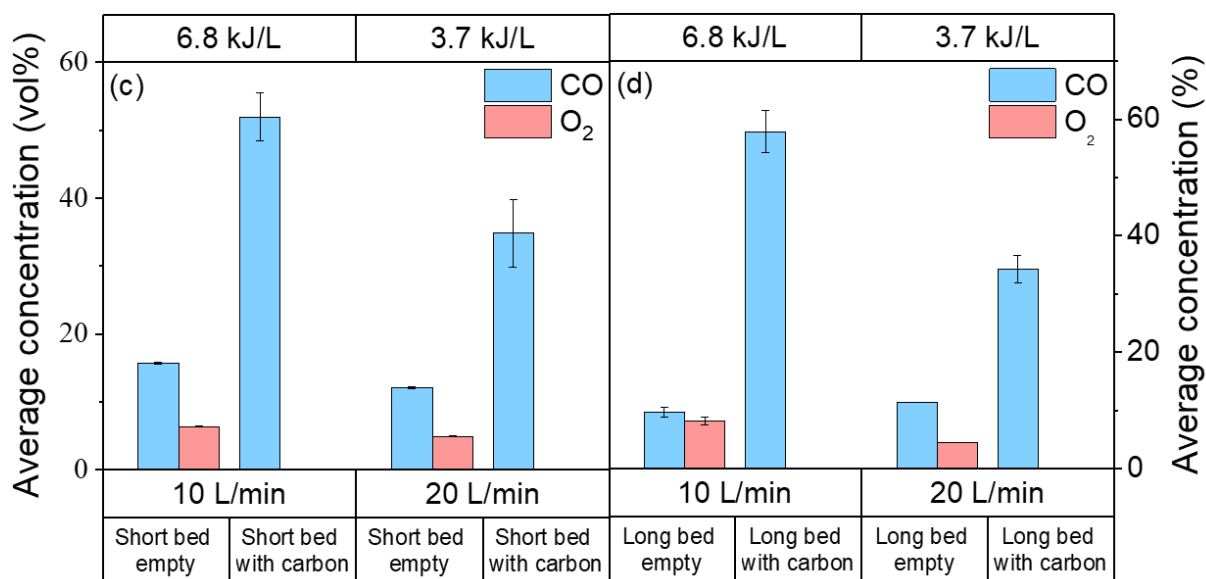


Fig. 3. Comparison of average CO₂ conversion for the (a) short and (b) long beds, as well as the corresponding CO and O₂ concentrations (c, d), when empty and filled with carbon, at high (6.8 kJ/L) and low (3.7 kJ/L) SEI values.

The empty bed conversions are in the range of previously obtained results using unmodified warm plasma setups, ca. 8-15 % [9,10,31]. The conversion obtained with the empty long bed increases with decreasing SEI (from 8.4 % at 6.8 kJ/L to 9.9 % at 3.7 kJ/L), an effect not observed with the short empty bed and not typical for similar unmodified setups, where the conversion typically rises with SEI. The drop at higher SEI is likely due to some gas recirculation occurring further into the long bed, past the metallic mesh-covered openings where the gas exits the bed (see Fig. 2a). This yields some recombination of the products, back into CO₂, explaining the lower conversion, and this effect is enhanced at higher SEI due to the reduced convective transport along the bed at the lower flow rate. In the lower SEI case, the higher flow rate promotes the removal of the produced CO out of this high temperature recombination zone, preventing the formed CO recombining with O/O₂ and resulting in a higher CO₂ conversion of nearly 10 %.

In the experiments with carbon packed into the beds, two distinctly different trends can be observed in the average conversion plots for the short and long beds, correlated to the two SEI conditions. At high SEI (i.e., lower flow rate, represented by the orange columns in Fig. 3a and Fig. 3b) **Fig. 3**, a clear difference in conversion is present. The short bed results in a lower conversion than the long bed, with an average value of 34 % compared to 41 %. In both beds, CO is formed from three key overall reaction pathways with carbon outlined in the introduction (Eq. 1-3). If we assume that the combined oxygen concentration (atomic + molecular) entering the carbon bed is approximately equal to the values detected downstream in the absence of carbon (i.e. empty beds, Fig. S4a and Fig. S4b), we can predict O₂ concentrations in the range of 4 – 7 vol% entering the bed. In reality, these values may be slightly higher, as recombination of CO and O/O₂ to form CO₂ has a limited time to occur in the case of a filled carbon bed. If we conservatively estimate 10 vol% O₂ entering the bed, this will result in the production of approximately 20 vol% CO. While these values are not insignificant compared to the total CO formed (ca. 52 vol% for the short bed and ca. 58 vol% for the long bed) at this high SEI condition, it is clear that the majority of CO formed still occurs via Eq. 3, i.e., the RBR. This endothermic reaction requires temperatures above 1000 K to proceed at an appreciable rate at atmospheric pressure [18,19]. As such, a flux of heat and reactant species (CO₂) are key components required for this reaction to occur [32]. In the case of the long bed at high SEI, more heat from the plasma chamber is retained within the bed compared to the short bed. In the short bed, heat is rapidly transported out through the mesh-covered openings in the side walls, as shown schematically in Fig. 2(b). The additional length of the long bed means that some of this ‘lost heat’ in the short bed is transported further into the bed, heating the carbon and accelerating the RBR. In addition, the diffusive flux of CO₂ to the surface of the solid carbon pellets is higher in the long bed compared to the short bed at this SEI condition, as the extra volume allows for more carbon to be packed and an increased total surface area exposed

to the high temperature gas stream. Hence, at high SEI, the long bed clearly performs better than the short bed, for the above explained reasons.

Interestingly, the difference in conversion between the beds in the presence of carbon diminishes with decreasing SEI, as represented by the green columns in Fig. 3(a) and Fig. 3(b). Under these conditions, the short bed results in an average conversion of 20 % compared to 19 % for the long bed. As mentioned previously, the SEI reduction is achieved by increasing the flow rate and matching the power between the setups. This suggests that the flow rate becomes the dominant parameter at lower SEI values, reducing the effect of bed length variation on the process. As such, the convective heat transport out of both beds becomes approximately equal, resulting in similar amounts of carbon at the same temperature. The temperature at the carbon surface and in the gas phase further into the long bed likely reaches a lower value compared to the high SEI case, decreasing the rate of the RBR in this section of the bed. In this scenario, the first portion of the long bed is acting as the primary site for the RBR, with the length of this site being akin to the total length of the short bed. In addition, as the flow rate increases, the diffusive contribution of species flux will decrease in favour of convective transport out of the bed, reducing the significance of this parameter in the long bed and aligning the resulting conversion in the two beds.

For all SEI conditions applied to either the short or long bed in the presence of carbon, complete oxygen removal was achieved for the duration of the run (Fig. 3c and Fig. 3d). This is further highlighted in the plot of species concentrations detected at the outlet (see SI, Fig. S3a), wherein the detected O_2 concentration only rises above 0 % when the CO and CO_2 concentrations decrease and increase, respectively. This change occurred when over 97 % of the carbon was converted and the experiment was concluded soon after (see Table S1 in SI).

In summary, the best results are obtained for the long bed at high SEI, reaching a maximum CO₂ conversion of 41 % (see Fig. 3b). This improvement is approximately five-fold when compared to the long bed in the absence of carbon at this condition (8.5 %). Even more, the CO concentration increases from about 10% (without carbon) to nearly 60% at these conditions, a near six-fold improvement. A near-complete removal of O₂ produced from the plasma-based dissociation of CO₂ was observed during each experiment with carbonaceous material present in the bed (Fig. S3c and Fig. S3d). Importantly, the silo system, which did not work well in our previous work [18], now clearly functions efficiently, both due to the higher SEI achieved and the higher temperature realised within the bed (above the limit of K-type thermocouples, 1260 ° C) due to the use of a DC power supply (see Section 5.5 for further comparison between the works). This efficient operation allows for carbon consumed by oxidation (Eq. 1-2) and the RBR (Eq. 3) to be replenished and the process to run continuously until the majority of the 80 g of carbon loaded is consumed (>97 %). Obviously, if the silo capacity would be increased, so too would the duration of the process and sustained high conversion and EE. A theoretical limit to said silo increase is correlated to ash accumulation in the bed, which would eventually interrupt the carbon replenishment process. However, ash accumulation in this study was minimal and we do not foresee this as an issue under these specific experimental conditions (i.e. SEI values, bed length, carbon material).

5.1.2. Energy metrics

The energy performance of the short and long beds, in terms of both EE and EC, is compared in Fig. 4a and Fig. 4b.

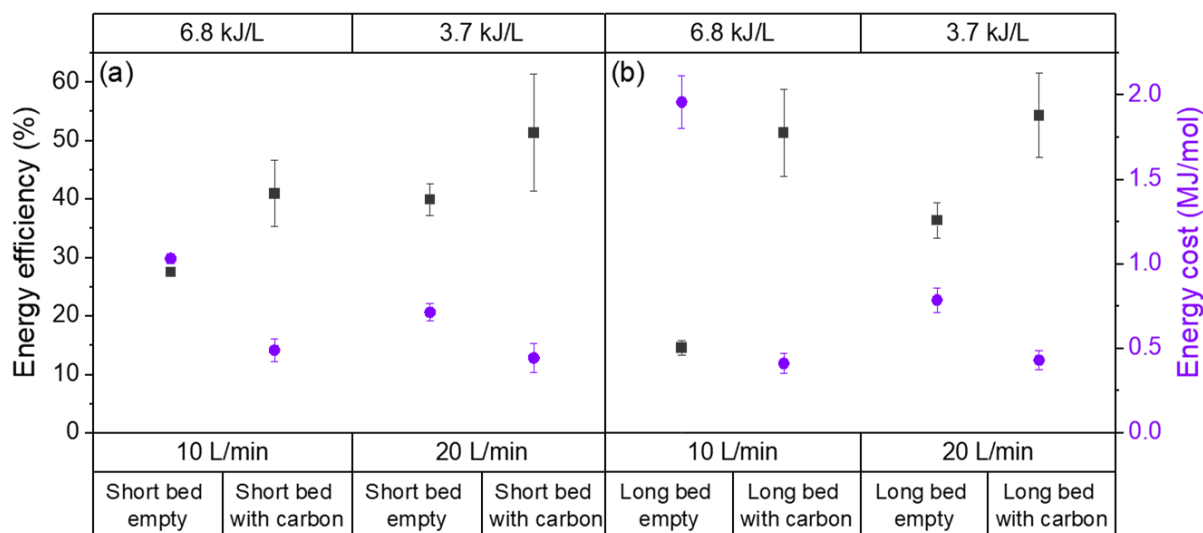


Fig. 4. Comparison of energy cost and energy efficiency for empty and filled (a) short and (b) long beds at high (6.8 kJ/L) and low (3.7 kJ/L) SEI values.

Fig. 4(a) shows the EC and EE obtained with empty and filled short bed, at the high and low SEI conditions. In general, the energy metrics greatly improve in the presence of carbon. For example, the EE at high SEI increases from 27 % to 41 % in the presence of carbon. This improved value is in line with the EE obtained at low SEI in the absence of carbon (40 %), but the EE rises further to ca. 51 % at this low SEI with carbon present. If we look at the same data points for EC, the same effect is realised at high SEI, with the EC decreasing more than two-fold from 1.03 MJ/mol for the empty bed to 0.49 MJ/mol for the packed bed. Interestingly, the alignment between the low SEI empty bed and high SEI filled bed is no longer retained, with the filled bed at high SEI achieving a lower EC than the empty bed at low SEI (0.71 MJ/mol). This discrepancy is a prime example of the misalignment between EE and EC that can occur in complex reaction systems. As mentioned previously, we advise the use of the simpler and more straightforward EC as the key energy metric, which indicates that the addition of carbon has a highly beneficial effect on the energy performance. The lowest EC with the short bed is obtained in the presence of carbon at low SEI, reaching 0.41 MJ/mol.

The EE and EC values obtained in the absence and presence of carbon in the long bed are shown in Fig. 4(b). The empty bed results align well with our previous results [18], showing an increase in EE (from 15 % to 36 %) and a drop in EC (from 1.96 MJ/mol to 0.79 MJ/mol) as a function of decreasing SEI. The high SEI empty long bed condition results in the highest EC of all conditions examined. Upon introduction of carbon, the energy performance improves significantly for both SEI conditions. The most dramatic improvement occurs at high SEI, with the EE increasing from 15 % to 51 % and the EC markedly decreases from 1.96 MJ/mol to 0.41 MJ/mol. Interestingly, the EE improves only slightly with decreasing SEI in the presence of carbon, rising to a value around 54 %. As the propagated error bars of the EE are quite large, these values can be considered approximately equal. This aligns with the resulting EC, with the value of 0.43 MJ/mol obtained at the lower SEI condition falling within the error of the high SEI result. Both energy metrics indicate that the effect of decreasing SEI has no significant impact on the energy performance of the long bed.

In summary, in combination with the conversion results of Fig. 3(b), the long bed filled with carbon produces the best results in terms of both optimum conversion (41 %) and EE/EC (51 % and 0.41 MJ/mol, respectively) at the high SEI of 6.8 kJ/L.

When comparing between the short and long bed in the presence of carbon, the EE for the long bed is higher (51 %) than for the short bed (41 %) at high SEI. This difference is due to the higher conversion at high SEI using the long bed (Fig. 3b). Interestingly, the relative contributions of the plasma-based CO₂ dissociation and the RBR to the EE vary significantly between the two beds at high SEI (see SI, Table S2). The conversion of 14 % obtained with an empty short bed is greater than with an empty long bed (8.4 %) (Fig. 3a and Fig. 3b), meaning $\alpha_{\text{Dissociation}}$ in the EE calculation (Eq. 11) is also greater for the short bed. This value lies around 0.4 for the short bed compared to just 0.23 for the long bed. As the enthalpy of CO₂ dissociation is greater than the reaction enthalpy for the RBR (283 kJ/mol vs. 172.5 kJ/mol), a

higher contribution factor for CO₂ dissociation ($\alpha_{\text{Dissociation}}$) leads to a higher EE of the short bed at high SEI. At low SEI, the similar conversion and contribution values for both beds result in near-equivalent EE values of 51 % and 54 % for the short and long bed, respectively.

As highlighted previously, EC is a more straightforward and simpler metric for determining the relative energy performance of such a complex reaction system. At high SEI, the results mirror those obtained for EE; the short bed configuration is less efficient at utilising the power deposited into the plasma when compared to the long bed. The short bed reaches an average EC of 0.49 MJ/mol, compared to 0.41 MJ/mol for the long bed at an SEI of 6.8 kJ/L. As this metric is solely determined by the conversion and SEI (Eq. 12), combined with the fact that the SEI values between the beds were approximately matched, this difference in EC is solely due to the improved conversion in the long bed at high SEI. The difference in EC can thus be attributed to the improved heat retention and species flux to the surface of the solid carbon in the long bed, as described above. At low SEI, the EC for both configurations approach similar values, i.e., 0.44 MJ/mol and 0.43 MJ/mol for the short and long bed, respectively. These energy metrics clearly indicate and reinforce our finding that the bed length is not a key parameter in determining the performance of a post-plasma carbon bed below a certain SEI threshold, when heat and species convective transport becomes the dominant factor in determining the bed efficiency. However, bed length is an important design parameter to consider at high SEI, due to the reduced convective heat and species transport out of the bed at this condition. Indeed, high SEI facilitates a higher bed temperature, promoting the RBR and enabling an EC minimum of 0.41 MJ/mol.

5.2. Effect of bed insulation

In order to utilise the heat produced in the plasma downstream (post-plasma), we designed an insulated carbon bed with the specific aim of retaining residual heat, which is otherwise lost to

the environment around the reactor. The time evolution profiles of CO₂ conversion obtained during a single run using the short, long and insulated beds are plotted in Fig. 5. The average conversion values, the produced CO and O₂ concentrations, EE, and EC for the insulated bed are compared in the supporting information (Section S4, Fig. S4 and Fig. S5).

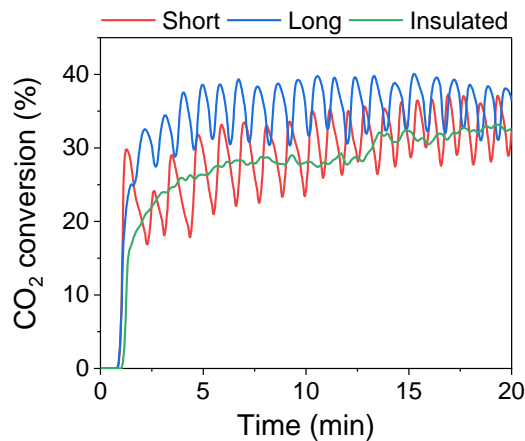


Fig. 5. Example conversion profiles obtained for the short, long and insulated beds, at SEI of 6.8 kJ/L. The fluctuations observed for the long and short bed are due to cold carbon entering the bed (see detailed explanation in the text).

A noticeable difference in the conversion profiles can be seen in Fig. 5, as the oscillations present in the short and long bed plots are markedly reduced in the plot for the insulated bed. The oscillation damping observed may be the result of two key differences between the bed configurations. Firstly, the insulated bed design incorporates the carbon feeding silo inside the reactor exhaust, meaning that the high-temperature gas exiting the reactor/carbon bed must also flow past the silo prior to exiting the reactor setup. This design feature leads to heating by the gas stream of the silo and carbon stored within. Essentially, this manifests as a heating system for the carbon loaded into the silo, utilising the “waste” heat from the plasma that would otherwise be released passively. Secondly, the insulated bed is designed with an anode extension (see Fig. 2c), meaning that the arc and its afterglow are not continuously impacted and interrupted by fresh carbon entering the bed, as may be the case with the short and long

beds. The former hypothesis of heating the silo and carbon is tested and described in section 5.4 below (Effect of heated silo). An in-depth analysis of the conversion and energy metrics obtained with the insulated bed can be found in the supporting information (Section S4).

5.3. Performance comparison of the different beds

A comparative overview of the EC versus conversion for all beds, both empty and filled, at low and high SEI can be seen in Fig. 6

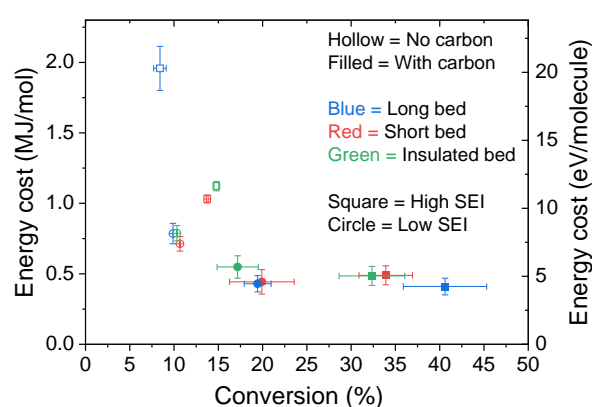


Fig. 6. Comparison of energy cost versus conversion for long (blue), short (red) and insulated (green) beds with carbon (filled symbols) and without carbon (hollow symbols) for the two experimental SEI conditions (low SEI = squares, high SEI = circles).

Under every experimental condition examined, the addition of carbon resulted in a significant improvement to the conversion whilst simultaneously decreasing the EC. At the low SEI condition (circles), the EC and conversion without carbon for all three beds was approximately equal (ca. 0.75 MJ/mol and 10 %). This trend was maintained in the presence of carbon, with each bed resulting in a lower EC around 0.5 MJ/mol and a corresponding improved CO₂ conversion in the range of 17 to 20 %. The high SEI condition (squares) produced a greater difference between the beds, both with (filled) and without (hollow) a carbon loading. The short (red) and insulated (green) beds performed approximately in-line with each other,

resulting in halving of the EC from ca. 1 MJ/mol to 0.49 MJ/mol in the presence of carbon. This improved energy performance was accompanied by a more than two-fold increase in conversion, from ca. 14 % to 34 %. As highlighted in the in-depth analysis of the performance of the insulated bed (SI, Section S4), the insulated bed volume and length is comparable to that of the short bed. This similarity likely results in approximately equal heat and species flux into and out of the bed, resulting in the alignment of EC and conversion between these two beds. The largest improvement, which coincides with the best results obtained in this study, occurred at high SEI (squares) for the long bed (blue). The highest EC and lowest conversion were realised in this bed in the absence of carbon (ca. 2 MJ/mol and 8.5 % respectively). This poor performance was drastically improved once carbon was loaded into the bed, with the EC reducing more than four-fold to 0.41 MJ/mol (ca. 100 eV/molecule) and the conversion increasing nearly five-fold to 41 %. Evidently, the implemented post-plasma carbon beds were effective for reducing the EC of the process in addition to increasing the conversion. Importantly, this effect was amplified at high SEI, with the long bed (blue) outperforming the short (red) and insulated (green) beds for both of the key metrics. This insight suggests that carbon bed length should be proportional to the input variable of SEI, especially at higher SEI values.

5.4. Effect of a heated silo

The absence of large oscillations of the process performance (as reflected by the CO₂ conversion profile in Fig. 5 **Fig. 5**) when using the insulated carbon bed leads to the hypothesis that said oscillations are caused by the cold carbon entering the bed from the external, non-heated silo, in case of the long and short carbon beds (see Fig. 2a and Fig. 2b, respectively). As such, we applied external heating to the silo to test this effect. Fig. 7 shows an example of conversion profiles obtained with the long bed at high SEI (6.8 kJ/L).

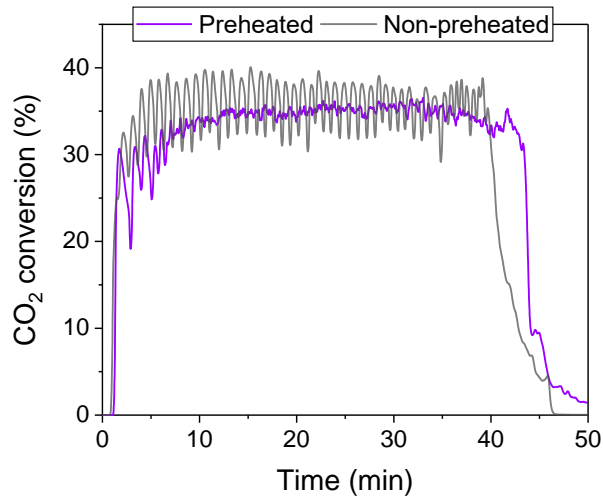


Fig. 7. Conversion profiles for the long bed with and without pre-heating of the external filled silo at high SEI (6.8 kJ/L).

The dramatic oscillations present without pre-heating (blue) are significantly reduced in the case of pre-heating the external silo (black). While the profiles differ greatly, the average conversion values remain virtually constant within the steady-like state timeframe (see SI, Fig. S3b), with a value around 39 % for the pre-heated case versus 40 % for the non-preheated silo. Naturally, the EE and EC values also remain approximately equal (ca. 46% and 0.49 MJ/mol, respectively, for the heated scenario).

In actuality, reactor design improvements with heat recovery from the post-plasma chamber could be applied to the silo to allow for energy cost calculation directly from the plug or plasma-deposited power (such as in the insulated bed design). However, at our initial experimental stage, we should include the energy required to heat the carbon in the silo into the energy cost of the process to allow accurate metrics estimation (Eq. 14).

$$Q [J] = m [kg] * C_p [J/(kg * K)] * \Delta T [K] \quad (14)$$

Q is the heat required to change the temperature of a substance by the amount equal to ΔT , m is the mass of the substance and C_p is the specific heat capacity. If we assume that the 80 g of carbon in the silo reaches a temperature of 150 °C (to which the heating tape was set), with the

heat capacity of carbon as $1.1 \text{ J/g}\cdot^\circ\text{C}$ and the molar mass of activated carbon equal to 12.01 g/mol , then the energy required amounts to approximately 1.7 kJ/mol . This small figure lies within the error margin of the EC calculation for the process, indicating the minor impact it has on the final EC figure.

Even with these considerations, some minor oscillations in the pre-heated conversion profile remain, indicating that the heated silo is the major (but not the sole) reason for the insulated bed removing the oscillations observed with the short and long counterparts. The disruption of the arc and afterglow by fresh carbon entering the bed is likely the secondary, less significant cause of the oscillations. In the current short and long bed designs, the connection between the bed and the silo is positioned close to the reactor outlet, meaning that the carbon dropping into the bed falls directly into the path of the arc/afterglow. Unfortunately, this disruption cannot be determined from the monitored electrical properties of the arc (e.g. using the voltage to determine the change in the arc length) due to the stochastic nature of the takeover mode in which the arc operates (see SI, Fig. S1). Further clarification of this effect could be achieved by redesigning the bed and external silo coupling to be as far into the bed as possible from the reactor outlet (see graphical example in SI, Fig. S6).

Overall, although the insulated carbon bed and its integrated, inherently heated silo perform slightly worse than the optimum long bed used in this study, their design and employment aided the identification of a simple method for reducing performance oscillations. While such oscillations are manageable industrially, they would incur additional costs at the product separation stage (e.g. requiring large buffer vessels, increased reactor container footprint). As evidenced in our work, these extra detractors can be bypassed by implementing simple heat recovery for heating the carbon silo (either integrated or external).

5.5. Comparison with state-of-the-art

An overview of the process metrics derived from the currently available literature implementing a post-plasma carbon bed is compiled in Table 1. The conditions resulting in the highest conversion were elected as the condition of interest, with the EE and EC values taken at this condition. It should be noted that these metrics often did not align (i.e. highest conversion not obtained with the highest EE/lowest EC), unlike in our work wherein the optimum conversion (41 %) and EE/EC (51 % and 0.41 MJ/mol) were obtained with the same carbon bed (long) at the same SEI condition (6.8 kJ/L).

The works with over-estimated EE due to neglecting the contribution of the lower enthalpy RBR are indicated “^(a)” along with those underestimating the EE due to overestimation of the RBR contribution “^(b)”. If data is presented in these works for the conversion in the absence of carbon, the EE has been re-calculated “^(c)” to allow direct comparison with our work. If CO₂ was diluted with a secondary gas (e.g. Ar) “^(d)”, the absolute conversion is listed, with the effective conversion shown in parentheses. If V_m wasn’t stated in the publication, the SEI was converted from kJ/L to eV/molecule assuming a standard molar volume of 24.06 L/mol (293 K and 1 atm) as used in this work.

The works of Liu et al. (Entry #2) and Li et al. (Entry #3) report energy metrics in terms of CO output, resulting in higher EE and lower EC compared to electing CO₂ as the molecule of interest. These values have been recalculated in relation to converted CO₂ to align with this and other published works.

Table 1 Overview of published post-plasma carbon bed results, compared with our work.

Entry #	Plasma reactor type	CO ₂ flow rate (L/min)	Specific energy input		CO ₂ conversion (%)	Energy		Ref.
			(kJ/L)	(eV/mlc)		Cost (MJ/mol CO ₂)	Efficiency (%)	

1. ^a	MW plasma	10	24	5.99	40	1.44	14	Uhm <i>et al.</i> [19]
2. ^{a,d}	DC thermal plasma	26	19	4.71	95 (48)	0.94	30	Liu <i>et al.</i> [20]
3. ^{a,d}	DC thermal plasma	23	20	4.99	93 (46)	1.06	27	Li <i>et al.</i> [21]
4. ^b	DC GA	4	7.5	1.87	21	0.85	24	Huang <i>et al.</i> [22]
5. ^b	DC GAP	5	5.5	1.37	27	0.48	37 (41 ^c)	Zhang <i>et al.</i> [23]
6. ^a	AC GAP	10	3.2	0.81	13	0.62	45 (39 ^c)	Girard-Sahun <i>et al.</i> [18]
7. ^{a,d}	MW plasma	4.8	18	4.18	75 (60)	0.67	30 (29 ^c)	Wu <i>et al.</i> [24]
8.	DC GAP	10	6.8	1.70	41	0.41	51	This work

^aOverestimated EE

^bUnderestimated EE

^cCorrected EE in parentheses

^dEffective conversion in parentheses

We specifically focus on three parameters as performance criteria: 1) CO₂ conversion, 2) EC, and 3) EE (albeit more ambiguous than EC). For each of the entries shown (except Uhm *et al.* – no data available), O₂ was completely removed from the effluent stream in the presence of carbon, demonstrating the potential of a post-plasma carbon bed for producing an O₂-free effluent stream. In our study (Entry #8), the best results (obtained using the long bed) have improved upon the conversion as well as both energy metrics in comparison to other warm plasma setups reported in literature (Entries #1 and #4-7). In terms of SEI, the most comparable work was carried out by Huang *et al.* (Entry #4), wherein the authors achieved a peak conversion of 21 % at an EC of 0.74 MJ/mol. We observe a near two-fold improvement in

conversion and EC in our work. Girard-Sahun *et al.* (Entry #6) used a similar setup to the long bed configuration used in our work, albeit with an AC PSU. Our conversion is improved by more than a factor of three (from 13 % to 41 %), while the EC is also reduced significantly (from 0.57 MJ/mol to 0.41 MJ/mol). This difference is likely due to the higher SEI applied in our work, in addition to the use of a DC PSU, which enables a higher temperature within the carbon bed and facilitates an enhancement of the RBR. Moreover, we report average conversion and EE/EC values which can be maintained (within the error margins) for a notably longer plasma operation time (order of 1 hour), due to the continuous supply of fresh carbon from the silo. This was not the case in the work of Girard-Sahun *et al.* [18], where the performance enhancement of the carbon bed was only obtained for a few minutes.

If we contrast Girard-Sahun's results with those obtained at low SEI (3.7 kJ/L) in our study, our setup still performs better, with a conversion of 19 % versus 13 % realised in their work. An EC comparison at these conditions supports the improvement, reaching a low EC of 0.43 MJ/mol compared to 0.57 MJ/mol achieved previously. As the SEI was approximately equal for these results, the difference arises primarily due to the PSUs used. The DC PSU in our study leads to a higher post-plasma temperature compared to the AC PSU, due to the constant electrode polarity [26], demonstrating that the type of PSU can also significantly affect the performance.

In the studies with MW plasma reactors, Uhm *et al.* (Entry #1) obtained a conversion similar to our work (ca. 40 %), albeit with a significantly higher EC of 1.3 MJ/mol. More recently, Wu *et al.* (Entry #7) reported a higher (absolute) CO₂ conversion (75 %) than our work, but also required an elevated EC (0.72 MJ/mol) to achieve this result. Importantly, however, this study diluted the CO₂ inlet gas stream with argon, and was thus reporting absolute conversion instead of the more correct effective conversion, which accounts for the multi-component inlet mixture [29]. The effective conversion obtained (60 %) was still higher than the conversion obtained in

this work due to the high SEI (18 kJ/L) applied to the MW reactor. This value is more akin to that used in thermal plasma systems (Entries #2-3), which has a positive effect on conversion but clearly sacrifices the energy performance. In contrast, our system reaches a peak conversion and minimum EC (and maximum EE) at the same SEI.

When comparing our results with those obtained using thermal plasma systems (Entries #2 and #3), a clear difference in conversion is present. Both studies required Ar dilution of the inlet CO₂ stream to operate and reported absolute conversions up to 95 %, while the more correct effective conversion values were decidedly lower. For example, the effective conversions obtained by Liu (Entry #2) and Li (Entry #3) would be equal to 48 % and 46 %, respectively. These values are more representative of the CO₂ conversion in relation to the total inflow gas stream. Similar to the high SEI case of Wu *et al.*, a higher EC is required to obtain these higher reported conversions.

As evidenced by the recalculated variability in EE in Entries #4-6 and the indicated overestimated EE of Entries #1-3, EE is a difficult metric to calculate accurately in a relatively complex system, such as a post-plasma carbon bed. While our recalculation and derivation addition to the work of Zhang *et al.* provides a more realistic overview, the metric of EC is a far more consistent definition for the energy performance of the system. This definition can only vary depending on the power measurement and the molecule of interest. In each case in the table (including our work), the power used in the EC calculation is the plasma-deposited power. A more industrially relevant power measurement would be the total power, also known as “plug power”, which accounts for power requirements of the PSU, chillers and other electrical components (e.g. ballast resistors) of the system. In terms of the molecule of interest, the EC values shown in the table correspond to the molar quantity of the CO₂ input.

6. Conclusions

We presented various post-plasma carbon bed designs for enhancing CO₂ conversion. The bed length has an impact on conversion and EC at high SEI (6.8 kJ/L, 1.7 eV/molecule), with the longest bed reaching a maximum conversion of 41 % with a minimum EC of 0.41 MJ/mol and maximum EE of 51%. At a lower SEI of 3.7 kJ/L (0.97 eV/molecule), the short and long beds produce similar results in conversion and EC (ca. 20 % and 0.43 MJ/mol, respectively). An external silo for continuous carbon supply was successfully implemented, enabling sustained high average conversion and energy metrics for extended periods (order of 1 hour). The effect of additional insulation of the bed has a negligible impact on the average performance but the innovative integrated silo system implemented real-time heat recovery in the form of heating the carbon residing in the silo system. This recovery resulted in the removal of oscillations in the conversion profile, providing a more stable and consistent output to the process. Pre-heating of the external carbon silo was tested, yielding a similar smoothed conversion profile to the insulated bed and thus highlighting the importance of pre-heating the carbon prior to entering the bed/reaction zone. Furthermore, we presented an updated formula for the calculation of EE, which emphasises the variability of this metric, as also reflected by the comparison of the state-of-the-art carbon bed works. In such a scenario, Occam's razor should be reflected upon, and we therefore advocate for the use of the more straightforward metric of EC as the primary method of energy comparison between post-plasma carbon bed systems. Last but not least, we conducted an in-depth comparison with current state-of-the-art post-plasma carbon bed setups, demonstrating the drastic improvement obtained with our setup (long bed, high SEI) by achieving both high conversion (41 %) as well as the lowest EC (0.41 MJ/mol) and highest EE (51%) reported to-date, that coincide at the same SEI.

CRedit authorship contribution statement

Colin O'Modhrain: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Project administration, Resources, Writing – original draft, Writing – review & editing. *Yury Gorbanev*: Conceptualization, Data curation, Project administration, Supervision, Writing – review & editing. *Annemie Bogaerts*: Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] B. M. Tackett, E. Gomez, and J. G. Chen, *Nature Catalysis* 2 (2019) 381-386
- [2] J. Gao, S. Choo Sze Shiong, and Y. Liu, *Chemical Engineering Journal* 472 (2023)
- [3] O. Gutiérrez-Sánchez, B. Bohlen, N. Daems, M. Bulut, D. Pant, and T. Breugelmans, *ChemElectroChem* 9 (2022)
- [4] G. Wang, J. Chen, Y. Ding, P. Cai, L. Yi, Y. Li, C. Tu, Y. Hou, Z. Wen, and L. Dai, *Chem Soc Rev* 50 (2021) 4993-5061
- [5] S. Patial, R. Kumar, P. Raizada, P. Singh, Q. Van Le, E. Lichtfouse, D. Le Tri Nguyen, and V. H. Nguyen, *Environ Res* 197 (2021) 111134
- [6] Y. Li, Y. Wei, W. He, Z. Tang, J. Xiong, and Z. Zhao, *Chinese Chemical Letters* 34 (2023) 108429
- [7] V. Longo, G. Centi, S. Perathoner, and C. Genovese, *Current Opinion in Green and Sustainable Chemistry* 46 (2024) 100893-100993

- [8] R. Snoeckx and A. Bogaerts, *Chem Soc Rev* 46 (2017) 5805-5863
- [9] A. Bogaerts and G. Centi, *Frontiers in Energy Research* 8 (2020)
- [10] R. Vertongen and A. Bogaerts, *Journal of CO2 Utilization* 72 (2023) 102510-102531
- [11] M. Ramakers, G. Trenchev, S. Heijkers, W. Wang, and A. Bogaerts, *ChemSusChem* 10 (2017) 2642-2652
- [12] A. Hecimovic, F. A. D'Isa, E. Carbone, and U. Fantz, *Journal of Co2 Utilization* 57 (2022) 1-8
- [13] E. R. Mercer, S. Van Alphen, C. F. A. M. van Deursen, T. W. H. Righart, W. A. Bongers, R. Snyders, A. Bogaerts, M. C. M. van de Sanden, and F. J. J. Peeters, *Fuel* 334 (2023)
- [14] A. Hecimovic, C. K. Kiefer, A. Meindl, R. Antunes, and U. Fantz, *Journal of Co2 Utilization* 71 (2023) 102473-102481
- [15] R. Antunes, K. Wieggers, A. Hecimovic, C. K. Kiefer, S. Buchberger, A. Meindl, T. Schiestel, A. Schulz, M. Walker, and U. Fantz, *Acs Sustainable Chemistry & Engineering* 11 (2023) 15984-15993
- [16] R. García, C. Pizarro, A. G. Lavín, and J. L. Bueno, *Fuel* 195 (2017) 182-189
- [17] S. Ullah, S. S. A. Shah, M. Altaf, I. Hossain, M. E. El Sayed, M. Kallel, Z. M. El-Bahy, A. U. Rehman, T. Najam, and M. A. Nazir, *Journal of Analytical and Applied Pyrolysis* 179 (2024) 106480-106510
- [18] F. Girard-Sahun, O. Biondo, G. Trenchev, G. van Rooij, and A. Bogaerts, *Chemical Engineering Journal* 442 (2022) 136268-136284
- [19] H. S. Uhm, H. S. Kwak, and Y. C. Hong, *Environ Pollut* 211 (2016) 191-7
- [20] P. Liu, X. S. Liu, J. Shen, Y. X. Yin, T. Yang, Q. Huang, D. Auerbach, and A. W. Kleijn, *Plasma Science & Technology* 21 (2019)
- [21] Z. K. Li, T. Yang, S. J. Yuan, Y. X. Yin, E. J. Devid, Q. Huang, D. Auerbach, and A. W. Kleijn, *Journal of Energy Chemistry* 45 (2020) 128-134
- [22] J. Y. Huang, H. Zhang, Q. H. Tan, L. Li, R. Y. Xu, Z. M. Xu, and X. D. Li, *Journal of Co2 Utilization* 45 (2021)
- [23] H. Zhang, Q. H. Tan, Q. X. Huang, K. Y. Wang, X. Tu, X. T. Zhao, C. F. Wu, J. H. Yan, and X. D. Li, *Acs Sustainable Chemistry & Engineering* 10 (2022) 7712-7725
- [24] Y. Wu, S. Z. Li, Y. L. Niu, H. J. Yan, D. Z. Yang, and J. L. Zhang, *Journal of Physics D-Applied Physics* 56 (2023) 065201-065214
- [25] T. Nunnally, K. Gutsol, A. Rabinovich, A. Fridman, A. Gutsol, and A. Kemoun, *Journal of Physics D-Applied Physics* 44 (2011) 274009-274017
- [26] L. Fulcheri, F. Fabry, S. Takali, and V. Rohani, *Plasma Chemistry and Plasma Processing* 35 (2015) 565-585
- [27] S. A. Wutzke, E. Pfender, and E. R. G. Eckert, *Aiaa Journal* 5 (1967) 707-&
- [28] I. Tsonev, C. O'Modhrain, A. Bogaerts, and Y. Gorbanev, *Acs Sustainable Chemistry & Engineering* 11 (2023) 1888-1897
- [29] B. Wanten, R. Vertongen, R. De Meyer, and A. Bogaerts, *Journal of Energy Chemistry* 86 (2023) 180-196
- [30] C. O'Modhrain, G. Trenchev, Y. Gorbanev, and A. Bogaerts, *ACS Eng Au* 4 (2024) 333-344
- [31] F. A. D'Isa, E. A. D. Carbone, A. Hecimovic, and U. Fantz, *Plasma Sources Science and Technology* 29 (2020)
- [32] S. Lee, J. John, G. Park, and J. G. Kim, *Applied Composite Materials* 28 (2021) 529-557

Post-plasma carbon bed design for CO₂ conversion: Does size and insulation matter?

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Supporting information

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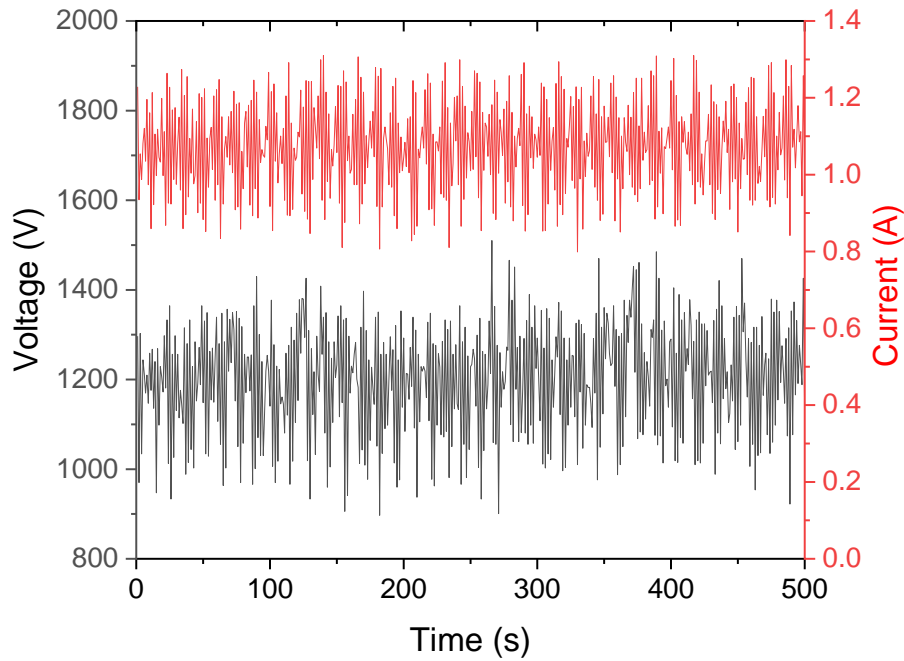
Section S1. Additional experimental details

The unit of flow rate was set according to the Bronkhorst standard litre per minute, which aligns with the standard EU definition taken at 293 K and 1 atm (molar volume = 24.06 L/mol). Due to the constriction of the reactor outlet, a reverse vortex flow pattern develops within the reactor chamber, as detailed in previous works from our group [1-3].

At the lower end of SEI (i.e. higher flow rate), the plasma may exhibit some restriking behaviour, increasing the random nature of the peaks and reducing the plasma stability. This was avoided as best as possible, resulting in some minor deviation in SEI between the configurations. The current was varied between the conditions and beds to allow for SEI matching, meaning that the ratio of power to flow rate was relatively constant between the beds.

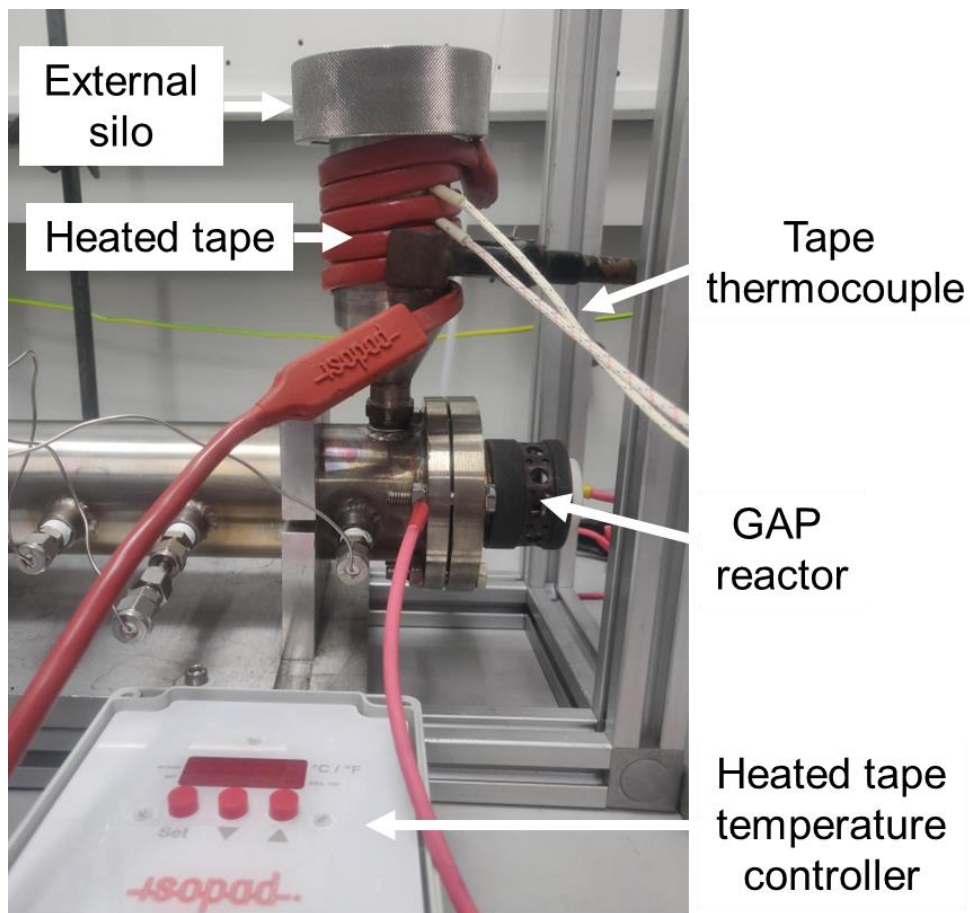
The outlet of each bed was equipped with a fine metallic mesh to keep carbon within. In addition, a small sacrificial mesh was placed over the anode to prevent carbon from entering into the reactor.

Fig. S1. An example oscillogram demonstrating the plasma operating in takeover mode



Electric arcs typically exist in one of three modes; steady, takeover and restrike [4]. In the steady mode, voltage and current fluctuations are minimal and the signal is relatively constant. In the takeover mode, more quasi-periodic fluctuations appear in the waveforms, as demonstrated in the figure above. Finally, the restriking mode is characterized by chaotic and non-periodic voltage and current temporal variations. In our experiments, the arc fluctuations (and hence voltage and current variations) were quasi-periodic, thus characterizing our mode of operation as the takeover mode.

Fig. S2. Experimental setup for heated external silo tests, implemented with the long carbon bed.



Section S2. Formulae for energy efficiency derived by Huang *et al.* [5] and Zhang *et al.* [6]

Huang *et al.* and Zhang *et al.* derived the following formulae to determine the contribution of plasma-based CO₂ dissociation and reverse Boudouard reaction (RBR) towards the calculation of energy efficiency (EE) of the system. The oxygen balance was used to determine said contributions.

$$\alpha_{CO_2 \text{ dissociation}} (\%) = \frac{2 * y_{O_2}^{out}}{2 * y_{O_2}^{out} + \frac{1}{2} * (y_{CO}^{out} - 2 * y_{O_2}^{out})} * 100\% \quad (SE1)$$

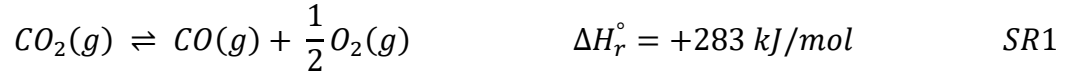
$$\alpha_{RBR} (\%) = \frac{\frac{1}{2} * (y_{CO}^{out} - 2 * y_{O_2}^{out})}{2 * y_{O_2}^{out} + \frac{1}{2} * (y_{CO}^{out} - 2 * y_{O_2}^{out})} * 100\% \quad (SE2)$$

In these equations, the factor α represents the contribution of the relative reaction shown in subscript (value = 0-1) and γ represents the fraction of the component indicated in subscript (i.e. CO₂/CO/O₂) detected at the outlet.

If the fraction of O₂ detected at the outlet is equal to zero, as is often the case in works regarding post-plasma carbon beds, then the contribution of plasma-based CO₂ dissociation ($\alpha_{CO_2 \text{ dissociation}}$, SE1) also becomes zero. This results in the standard reaction enthalpy of the RBR being the sole reaction contributing to the calculation of EE, which results in an underestimation ($\Delta H_{r \text{ RBR}}^\circ < \Delta H_{r \text{ CO}_2 \text{ dissociation}}^\circ$).

Section S3. Numerical example of energy efficiency calculation, showing the effect of various assumptions

Two main reactions contribute to the conversion of CO₂ in a system incorporating a post-plasma carbon bed, i.e., the plasma-based decomposition of CO₂ (SR1), and the RBR (SR2):



Additionally, three more reactions can occur between the oxygen produced by the CO₂ plasmolysis and the carbon present inside the bed.



In Section 3 in the main text, we made the assumption that only reaction SR3 occurs and the contribution of SR4 is negligible. The following example will demonstrate the influence of this assumption on the conversion and energy efficiency. In both cases, SR5 is assumed to be occurring in equal amounts at a specific SEI. As such, this reaction has been neglected in the following examples.

Conversion

We assume an inlet flow rate of 10 L/min CO₂ and the following gas concentrations are detected in the effluent stream:

$$CO_2 = 60 \% \quad CO = 40 \% \quad O_2 = 0 \%$$

We also assume that one liter of CO₂ is converted due to the plasma, which corresponds to a plasma-based conversion of 10 %. In this scenario, we can calculate the amount of CO₂ converted by the RBR for two distinct cases.

Case 1: SR3 is dominant solid carbon oxidation with O₂ in the carbon bed

$$y_{CO_2}^{out} = 0.6 = \frac{y_{CO_2}^{out}}{y_{CO}^{out} + y_{CO_2}^{out} + y_{O_2}^{out}} = \frac{9 - \chi}{1 + 1 + 2\chi + 9 - \chi + 0} \Rightarrow \chi = 1.5 L$$

From the 9 litres of CO₂ left after conversion by the plasma, χ litres are converted by the RBR. One litre of CO was formed by the plasma, and one litre was formed via reaction SR3. 2χ more litres will be formed via the RBR. This results in 1.5 L of CO₂ converted by the RBR. This corresponds to a net total amount of CO₂ converted of 2.5 L, or 25 % (1 L from the plasma and 1.5 L from RBR). The same can be done for case 2:

Case 2: SR4 is dominant solid carbon oxidation with O₂ in the carbon bed

$$y_{CO_2}^{out} = 0.6 = \frac{y_{CO_2}^{out}}{y_{CO}^{out} + y_{CO_2}^{out} + y_{O_2}^{out}} = \frac{9 - \chi + 0.5}{1 + 2\chi + 9 - \chi + 0.5 + 0} \Rightarrow X = 2 L$$

The biggest difference is that the oxygen produced by the plasma reaction (SR1) does not produce CO, but CO₂. However, this case also results in a net total CO₂ conversion of 2.5 L (25 %): one litre removed by the plasma, 2 litres removed by the RBR, and half a litre produced by reaction SR4.

Energy efficiency

The energy efficiency can be calculated via the following formula:

$$EE(\%) = \frac{\chi_{total}(\%) * (\alpha_{Plasma} * \Delta H_{r,Plasma}^{\circ}(kJ/mol) + \alpha_{RBR} * \Delta H_{r,RBR}^{\circ}(kJ/mol))}{SEI (kJ/mol)}$$

Hence, the contribution of both the plasma and RBR to the total CO₂ conversion must be determined.

$$\alpha_{Plasma} = \frac{\chi_{plasma}(\%)}{\chi_{total}(\%)}$$

$$\alpha_{RBR} = 1 - \alpha_{Plasma}$$

Case 1:

$$\alpha_{Plasma} = \frac{\chi_{plasma}(\%)}{\chi_{total}(\%)} = \frac{1 L}{2.5 L} = 0.4$$

$$\alpha_{RBR} = 1 - \alpha_{Plasma} = 1 - 0.4 = 0.6$$

If we take the high SEI value, we get:

$$EE(\%) = \frac{25\% * \left(0.4 * \frac{283kJ}{mol} + 0.6 * \frac{172.5kJ}{mol}\right)}{\frac{164kJ}{mol}} = 33.1\%$$

Case 2:

Because the plasma-based CO₂ conversion facilitates reaction SR4 by being responsible for the production of oxygen, its contribution to the overall conversion will be lower.

$$\alpha_{Plasma} = \frac{\chi_{plasma}(\%)}{\chi_{total}(\%)} = \frac{1 L - 0.5 L}{2.5 L} = 0.2 \quad (39)$$

$$\alpha_{RBR} = 1 - \alpha_{Plasma} = 1 - 0.2 = 0.8 \quad (40)$$

This results in the following energy efficiency:

$$\Rightarrow EE(\%) = \frac{25\% * \left(0.2 * \frac{283kJ}{mol} + 0.8 * \frac{172.5kJ}{mol}\right)}{\frac{115kJ}{mol}} = 29.7\% \quad (41)$$

Depending on the assumption made, a difference of about 5 % can occur.

In reality a combination of both reaction SR3 and SR4 will occur simultaneously. However, detecting the specific reaction occurring would be highly complex and outside the scope of this work.

Fig. S3. Example of (a) CO₂, CO and O₂ concentration profiles during an experiment and (b) example of a conversion profile with the pseudo-steady-state region highlighted.

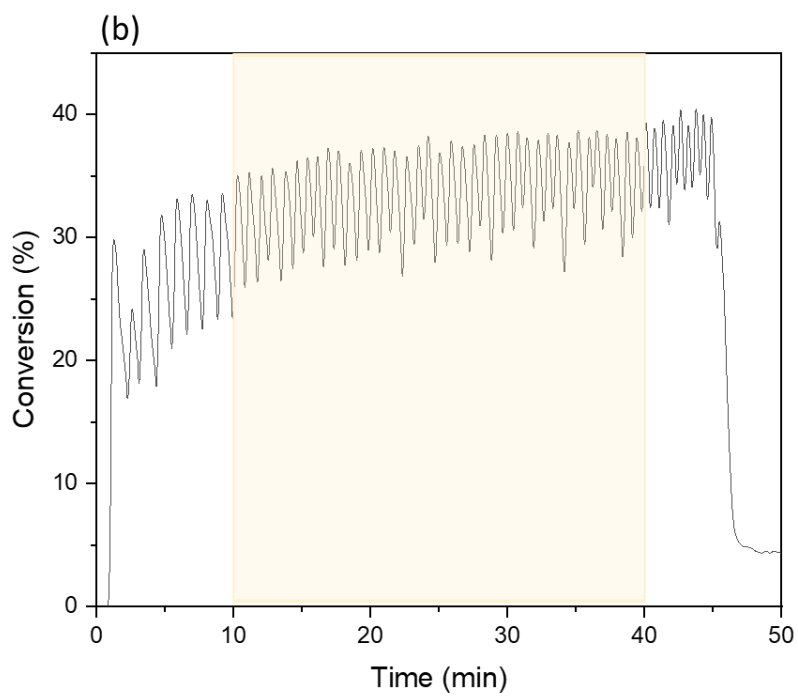
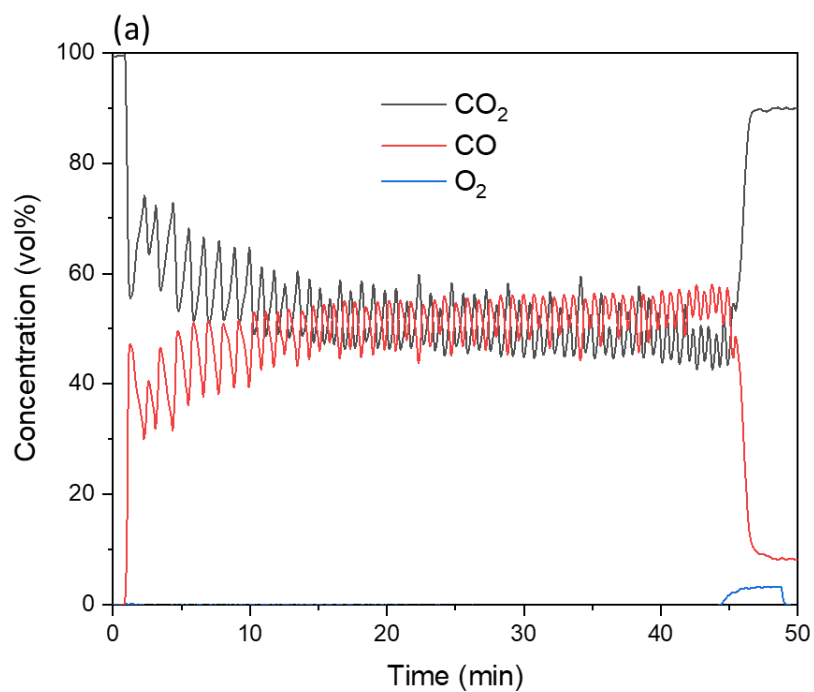


Table S1. Carbon loading and remaining post-reaction

Bed	Flow rate (L/min)	SEI (kJ/L)	Carbon loading (g)	Carbon remaining post-reaction (g)	Carbon reacted (%)
Short	10	6.8	80	2.3	97
	20	3.7		1.9	98
Long	10	6.8		2.5	97
	20	3.7		2.8	97
Insulated	10	6.8		2.2	97
	20	3.7		2.4	97

Table S2. Average contribution factors ($\alpha_{CO_2 \text{ dissociation}}$ & α_{RBR}) for all studied conditions

Bed	Carbon present?	Flow rate (L/min)	SEI (kJ/L)	$\alpha_{CO_2 \text{ dissociation}}$	α_{RBR}
Short	Y	10	6.8	0.40	0.60
	N	10	6.8	1.0	0.0
	Y	20	3.7	0.61	0.39
	N	20	3.7	1.0	0.0
Long	Y	10	6.8	0.23	0.77
	N	10	6.8	1.0	0.0
	Y	20	3.7	0.51	0.49
	N	20	3.7	1.0	0.0
Insulated	Y	10	6.8	0.48	0.52
	N	10	6.8	1.0	0.0
	Y	20	3.7	0.65	0.35
	N	20	3.7	1.0	0.0

Section S4. Analysis of insulated bed conversion and energy metrics

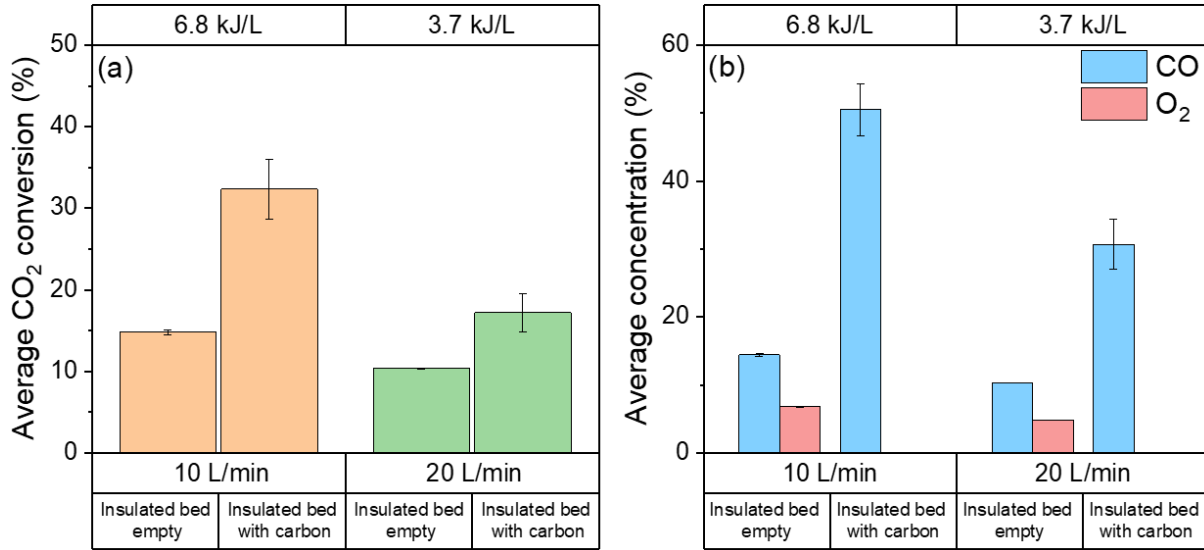


Fig. S4. Comparison of (a) average CO₂ conversion and (b) CO and O₂ concentrations for the insulated bed, when empty and filled with carbon, at high (6.8 kJ/L) and low (3.7 kJ/L) SEI values.

In terms of conversion, the insulated bed performs in-line with the short bed at high SEI (**Error! Reference source not found.**a above), reaching an average conversion of 32 % compared to 34 % obtained with the short bed. At low SEI, the values fall in-line with those obtained for both the short and long bed, with a slightly lower average value of 17 % (versus 20 % with the short bed and 19 % with the long bed). The slight reduction in conversion performance compared to the previous two beds is likely due to the fact that the plasma afterglow is not in direct contact with the carbon in the insulated bed. This change leads to a longer distance required for O/O₂ species to travel prior to interaction with the carbon, resulting in a larger extent of recombination of O/O₂ with CO instead of reacting with solid carbon [7,8]. In terms of the difference between high and low SEI, the insulated bed volume is similar to that of the short bed, meaning that the heat and species flux out of the reactor is more significant than with the long bed.

The performance enhancement is more pronounced at high SEI, yielding a factor two improvement in CO₂ conversion, and a factor three in CO concentration (Fig. 7b). Furthermore, the insulated carbon bed can also completely remove the produced O₂, both at high and low SEI (Fig. 7b), thus significantly reducing separation costs.

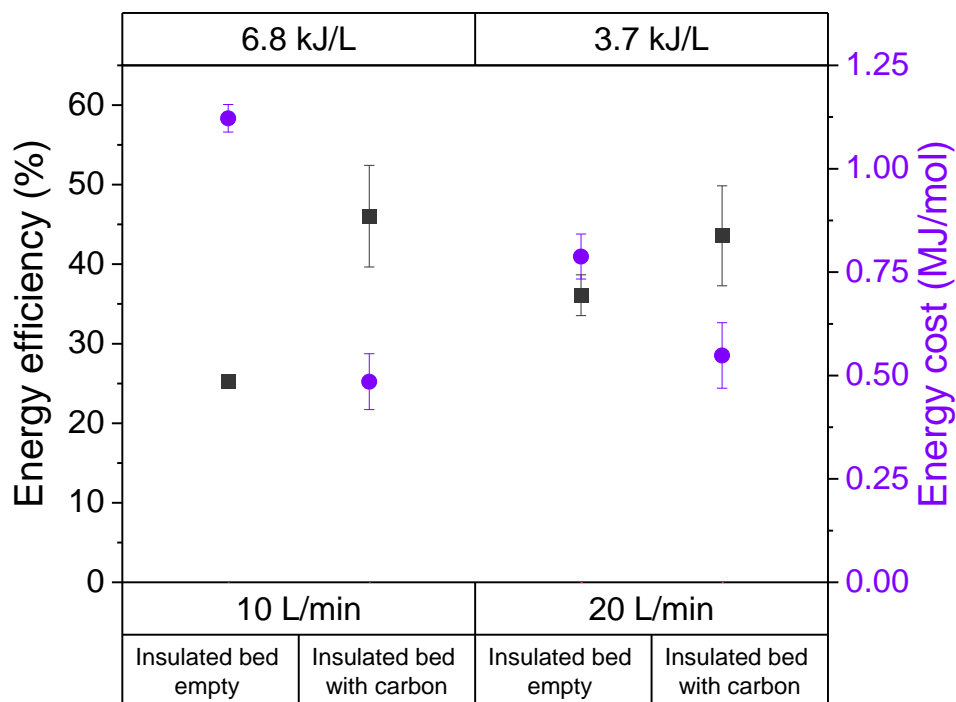


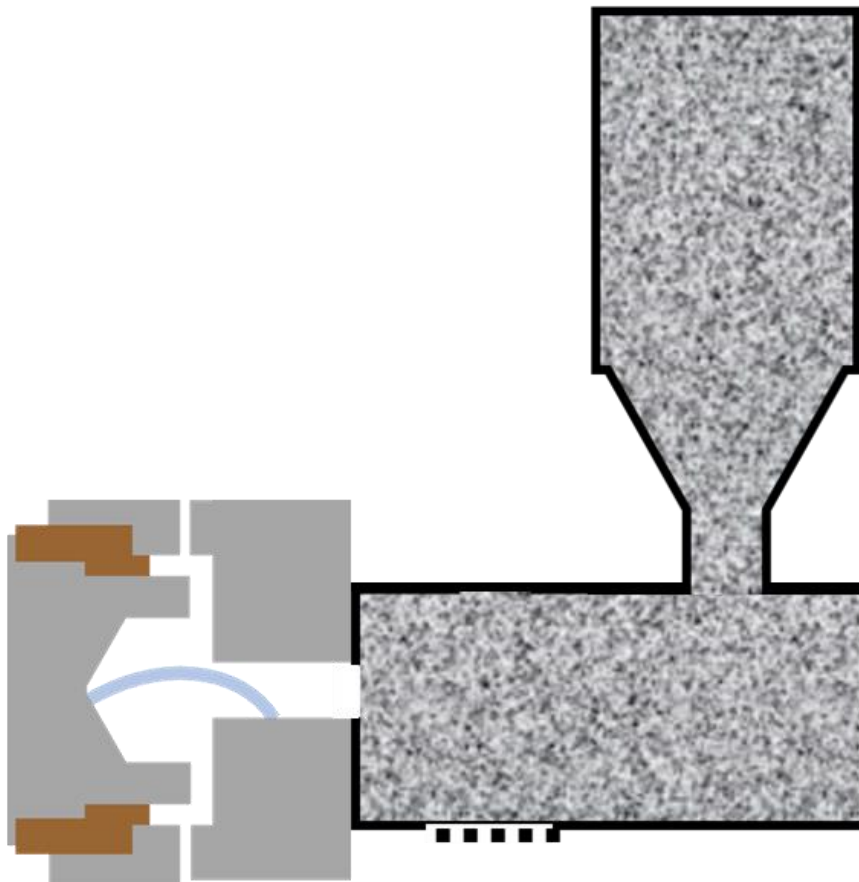
Fig. S5. Comparison of energy cost and energy efficiency between empty and filled insulated carbon bed at high (6.8 kJ/L) and low (3.7 kJ/L) SEI values.

The EE and EC of the insulated bed at high and low SEI conditions, for both empty bed and filled with carbon are plotted in Fig. . As observed with the short and long beds, the introduction of carbon results in improved energy metrics (both EE and EC) at the same SEI condition. Decreasing SEI in the presence of carbon reduces the performance marginally, resulting in a drop in EE from 46 % to 44 % and a rise in EC from 0.49 MJ/mol to 0.55 MJ/mol. This rise in EC (and drop in EE) is because the drop in conversion (from 32 % to 17 %) is relatively larger than the drop in SEI (see **Error! Reference source not found.** 12).

In comparison to the short and long beds, the insulated bed performs slightly better than the short bed at high SEI, reaching an EE of 46 % (compared to 41 %). This value is still below the maximum EE for the long bed (51 %) at high SEI. In terms of EC, both low and high SEI conditions with the insulated bed yield a higher value than the other two designs. The EC at high SEI is 0.49 MJ/mol, slightly higher than for the short bed. At low SEI, an EC of 0.55 MJ/mol is obtained, which is higher than for the other investigated configurations. This can be attributed to the lower conversion obtained with this bed at low SEI.

The discrepancy in EE and EC comparison between the short and insulated bed noticeable at high SEI is due to a multitude of minor differences in each of the variables required to calculate EE. Primarily, the CO₂ dissociation contribution (see SI, Table S1) in the insulated bed (0.46) is slightly higher than the same value in the short bed (0.4), which increases the EE. This difference in the relative values of EE and EC for the short and insulated beds further highlights the fact that calculating the EE in a multi-reactant system is heavily influenced by the variables, their derivation, and the assumptions therein. As such, EE is decidedly not the most suitable energy metric for accurately analysing the performance of a system containing a post-plasma carbon bed (and other complex multi-reactant systems such as plasma-based dry reforming of methane [9,10]). We advocate for the use of EC as the key metric for comparing energy performance results obtained within a study, and also between published works.

Fig. S6. Graphical example of potential long bed silo coupling redesign with aim of reducing fresh carbon impinging on plasma arc/afterglow.



References

- [1] R. Vertongen and A. Bogaerts, *Journal of CO2 Utilization* 72 (2023) 102510-102531
- [2] G. Trenchev, S. Kolev, W. Wang, M. Ramakers, and A. Bogaerts, *Journal of Physical Chemistry C* 121 (2017) 24470-24479
- [3] M. Ramakers, G. Trenchev, S. Heijkers, W. Wang, and A. Bogaerts, *ChemSusChem* 10 (2017) 2642-2652
- [4] S. A. Wutzke, E. Pfender, and E. R. G. Eckert, *Aiaa Journal* 5 (1967) 707-&
- [5] J. Y. Huang, H. Zhang, Q. H. Tan, L. Li, R. Y. Xu, Z. M. Xu, and X. D. Li, *Journal of Co2 Utilization* 45 (2021)
- [6] H. Zhang, Q. H. Tan, Q. X. Huang, K. Y. Wang, X. Tu, X. T. Zhao, C. F. Wu, J. H. Yan, and X. D. Li, *Acs Sustainable Chemistry & Engineering* 10 (2022) 7712-7725
- [7] F. A. D'Isa, E. A. D. Carbone, A. Hecimovic, and U. Fantz, *Plasma Sources Science and Technology* 29 (2020)
- [8] Y. Wu, S. Z. Li, Y. L. Niu, H. J. Yan, D. Z. Yang, and J. L. Zhang, *Journal of Physics D-Applied Physics* 56 (2023) 065201-065214
- [9] N. Pinhão, A. Moura, J. B. Branco, and J. Neves, *International Journal of Hydrogen Energy* 41 (2016) 9245-9255
- [10] B. Wanten, S. Maerivoet, C. Vantomme, J. Slaets, G. Trenchev, and A. Bogaerts, *Journal of CO2 Utilization* 56 (2022) 101869-101880