High-pressure CO\textsubscript{2} dissociation with nanosecond pulsed discharges

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Abstract
We investigate the conversion of CO\textsubscript{2} into CO and O\textsubscript{2} with nanosecond repetitively pulsed (NRP) discharges in a high-pressure batch reactor. Stable discharges are obtained at up to 12 bar. By-products are measured with gas chromatography. The energy efficiency is determined for a range of processing times, pulse energy, and fill pressures. It is only weakly sensitive to the plasma operating parameters, i.e. the extent of CO\textsubscript{2} conversion is almost linearly-dependent on the specific energy invested. A conversion rate as high as 14\% is achieved with an energy efficiency of 23\%. For long processing times, saturation in the yield and a drop in efficiency are observed, due to the increasing role of three-body recombination reactions, as described by zero-dimensional detailed kinetic modeling. The modeling reveals the presence of three-stage kinetics between NRP pulses, controlled by electron-impact CO\textsubscript{2} dissociation, vibrational relaxation, and neutral elementary kinetics. Transport effects are shown to be important for CO\textsubscript{2} conversion at high pressures. For fill pressures beyond 10 bar, CO\textsubscript{2} may locally transit into supercritical states. The supercritical plasma kinetics may bypass atomic oxygen pathways and directly convert CO\textsubscript{2} into O\textsubscript{2}. This work provides a detailed analysis of plasma-based high-pressure CO\textsubscript{2} conversion, which is of great relevance to future large-scale sustainable carbon capture, utilization, and storage.

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1. Introduction
The splitting of CO\textsubscript{2} and its conversion into value-added chemical feedstocks are one of several possible methods that can store electrical energy from renewable resources during off-peak demand periods. As a product of CO\textsubscript{2} splitting, CO is a combustible fuel. It can also be mixed with H\textsubscript{2} to produce synthesis gas (syngas), which is a compact, high energy-to-mass-ratio form for energy storage [1–3] and an energetic feedstock for manufacturing chemicals. CO\textsubscript{2} splitting finds other interesting applications such as in the processing of Mars resources [4], an example of which is in portable devices that can directly convert CO\textsubscript{2} in the Martian atmosphere into breathable O\textsubscript{2}.

The main challenge of this reforming process is the requirement to dissociate CO\textsubscript{2} with a high energy efficiency ($\eta$), i.e. the ratio of the dissociation enthalpy to the electrical energy invested, and a high conversion degree ($\Phi$), i.e. the fraction
of the original CO₂ in the feedstock that is converted to CO. For that, non-equilibrium plasma discharges are particularly suited as they are not bound by equilibrium thermodynamics. Figure 1 demonstrates the variation of η and ϕ with respect to reduced electric field E/N. Microwave (MW) plasma discharges (50–200 Torr) can have energy efficiencies that may be as high as 80% [5] with conversion degrees of up to 30%. The original explanation for such a high efficiency is the vibrational pumping and subsequent dissociation, although recently CO₂ thermal chemistry is shown to be critical [6, 7]. Other low-pressure plasmas such as radio-frequency (RF) [8] and direct current (DC) glow discharges [9, 10], have been used to study CO₂ splitting with varying degrees of energy efficiencies reported, but generally less than 15%.

While low-pressure plasma discharges may offer more favorable conditions to exploit non-equilibrium in the electron energetics, high-pressure discharges (such as those at atmospheric pressure or higher) may be more suitable for reforming applications because of their higher throughput and lower capital cost. However, the energy conversion efficiency for MW discharges appears to decrease with increasing pressure [5]. Studies carried out at atmospheric pressure show an efficiency limited to 20% [11] for a conversion degree of 10%. This decrease in efficiency is explained by the increase in losses due to vibrational–translational (VT) relaxation [12] at higher pressure. Recent results [13] suggest that the energy efficiency can be greatly increased (>90%) but at the cost of low conversion degree (2%), which offsets the higher throughput obtained with increased pressure. Other atmospheric pressure sources have been investigated, such as dielectric barrier discharges (DBDs) [14–16], which have reported conversion degrees of up to 35% but with energy efficiencies limited to 5%–8%. Using catalysts and packed-bed reactors [17–19], the energy efficiency of DBD splitting improves slightly, to 10%, while achieving a conversion degree of 20%. Other discharge splitting strategies have been reported, including the use of CO₂/N₂ or CO₂/Ar gas mixtures [20, 21] but the additives were not found to have a significant effect on the energy efficiency. Atmospheric pressure gliding arcs (GAs) [22–24] were reported to reach promising efficiencies comparable to those measured using sub-atmospheric MW discharges (η = 43%) with a conversion degree of 10% [23]. Nevertheless, scaling up GAs could be challenging due to issues related to plasma stability, electrode erosion, and heat dissipation.

Another promising candidate for the splitting of CO₂ at high pressures is nanosecond repetitively pulsed (NRP) discharges. Their short pulse width (~10 ns) and low duty cycle (1/1000) make them potentially energy efficient as most of the discharge energy resides in the electron fluid, which can participate in chemistry before thermalization with the background gas. These discharges can also be scalable with multi-needle structures of electrodes and concurrent initiation of multiple plasma streamers. They can be operated at conditions higher than atmospheric pressure for even greater reactant throughput. Studies of the dissociation of CO₂ mixtures using NRP discharges has been previously reported [25–29]. However, few prior studies exist on the splitting of pure CO₂ beyond atmospheric pressure conditions, where pressure-dependent decomposition and following quenching strategies such as mixing or cooling [30] are critical. One study carried out by Bak et al [31] in a flow reactor for pressures ranging from 2.4 to 5.1 atm reported energy efficiencies as high as 11.5%. From an energy balance analysis, the electronic excitation and auto-dissociation of CO₂ is suggested to be the dominant reaction pathway for CO formation. However, this work did not provide a direct connection between experimental measurements and kinetic modeling. How pressure-dependent reactions are coupled with the non-equilibrium electron energy transfer and plasma chemistry on the order of 10 bar is not well-understood, and is relevant for large-scale carbon capture, utilization, and storage projects [32].

To this end, we aim to study the NRP discharge splitting of CO₂ at high pressures (5–12 bar). In section 2, we describe the experimental setup, including the custom-fabricated high-pressure reactor (up to 125 bar) that accommodates a nanosecond pulsed discharge (up to 30 kV) across electrodes suitable for breakdown at high pressures. Here, we also describe the analysis of the product gases and the determination of the invested pulse energy. In section 3, we introduce our zero-dimensional chemical kinetics model and the high-pressure CO₂ dissociation reaction mechanism. In section 4, we present the experimental results including the measurements and quantification of the chemical products, and, using the kinetic analysis based on the reaction path flux, we discuss the predicted time evolution of energy and molecular conversion efficiency for CO₂ dissociation. The effects of pressure and deposited energy are discussed in detail in this section. In section 5, we offer conclusions. This work demonstrates a proof-of-concept plasma reactor for high-pressure CO₂ dissociation and provides understanding and insights for potential plasma-based large-scale carbon utilization projects, particularly those that operate at high pressures.
Figure 2. Process flow diagram for the high-pressure pulsed plasma discharge splitting studies.

2. Experimental setup

The high-pressure facility consists of a reactor chamber, a high voltage pulse generator, a high-pressure CO$_2$ supply system, a temperature control system, a gas chromatography (GC), and a vacuum pump (figure 2). The high voltage pulse generator (FID Technology Model F1112) delivers two signals of opposite polarities. Each signal has a maximum value of 15 kV, allowing the summary amplitude of 30 kV. The pulse duration is approximately 10 ns (FWHM) and the rise time is 5 ns. The pulse repetition frequency is variable but is held constant at 30 kHz for all the experiments reported here.

The reactor chamber is designed to sustain high pressures of up to 125 bar. The Sapphire windows are built into the chamber for optical access. Two feed-throughs provide electrical access for generating the discharge. The inner volume of the chamber, as designed, was 400 cm$^3$, but then reduced to 200 cm$^3$ by filling inert material (resin) to raise the conversion degree of CO above the detection threshold of the GC, as needed for the case of higher pressures.

2.1. Pin-to-plane electrode configuration

The electrode configuration consists of a pin-to-plane geometry. The pin electrode has a radius of curvature of approximately 10 µm. It is fabricated from tungsten wire using an electrochemical etching process as described in detail in appendix A. The initial gap distance $d_0$ is 150 ± 30 µm. The uncertainty originates from the uncertainty in the electrode length and is attributed to the electrode manufacturing process.

During the experiments, carbon deposition and slow degradation of the electrodes have been observed. The gap distance and the radius of curvature of the pin electrode increased, resulting in variations in the electric field, impedance, plasma volume, and deposited energy as discussed in section 2.3.

2.2. Product gas characterization

The product gases are analyzed by a Varian (Model 3400) GC, equipped with two columns (Molecular Sieve 5 Å and Porapak Q), and two non-destructive detectors in series, i.e. a thermal conductivity detector (TCD) and a pulsed discharge helium ionization detector (PDHID). The molecular sieve column can separate molecular oxygen (O$_2$) from molecular nitrogen (N$_2$), which allows us to ensure that there are no leaks in the system. Both the TCD and PDHID can detect O$_2$, CO, and CO$_2$, but have different sensitivity ranges. The TCD has a 1% resolution while the PDHID can detect mole fractions down to 100 ppm. In practice, a mole fraction of 0.5% is necessary to get reasonable quantitative data on CO. Appendix B details how we determine the conversion degree and the number density of CO molecules produced from the GC signals, considering the compressibility of CO$_2$ at high pressures.

2.3. Discharge energy measurements

Discharge energy measurements are performed with two high voltage probes (Tektronix P6015A, 75 MHz range) and a Rogowski current probe (Pearson 2877, 200 MHz, 2 ns rise time) connected to a Digital Oscilloscope (Tektronix TDS7104, 1 GHz). Energy measurements require synchronizing the probes with 0.1 ns precision. This is done by applying a high voltage pulse with a voltage $V < V_b$, i.e. less than the breakdown voltage of the CO$_2$ within the chamber. Synchronization depends on the response time of the different probes and the length of the cables, which are kept constant for all of the experiments reported here.

Figure 3(a) shows the typical current and voltage traces seen during an NRP discharge event in CO$_2$ at 5 bar, when a 20 kV (peak) voltage was applied between the two electrodes. The peak voltage, $V_{\text{max}}$, is lower than the open circuit voltage, $V_0$ (not shown) as the electrical resistance of the gap drops as
the gas breaks down, a process which begins (onset of conduction current, \( I_{\text{cond}} \)) before the application of the maximum voltage. From figure 3(b), the total energy deposited is measured to be 730 ± 50 µJ. The conduction phase starts after about 5 ns, when the total discharge current peaks at 11 A, and the conduction current eventually rises to 12 A (the displacement current, not shown, is then negative). A large fraction (95%) of the energy is deposited into the gas within the first 7 ns of the conduction phase. After 12 ns, the gap resistance is estimated to be <10 Ω and the voltage drop across the gap is small. The residual voltage and current peaks distributed regularly every 30 ns correspond to reflections of the initial pulse ringing in the 3 m transmission line. Although the total current is still fairly high, the voltage across the gap is too low (because of the relatively low plasma resistivity) to deposit any additional energy, and the total cumulative energy deposited within the discharge levels off.

The total deposited energy is found to increase slightly with each new pulse throughout an experiment of duration (processing time) of about 240 s. This drift at a typical experimental condition is shown in figure 4. We see that the energy per pulse increases over time by an amount of almost 50 µJ in a span of 240 s. It is attributed to electrode erosion as discussed in section 2.1. The gap distance was found to increase from the initial 150 µm–250 µm after 240 s, which led to a decreased electric field (below the initial breakdown field). Nonetheless, the reduced electric field \( E/N \) is maintained as the high discharge frequency induces residual heating. The total uncertainty in the pulse energy is comprised of both shot-to-shot fluctuations (on the order of 10 µJ) and the drift of any single pulse (e.g. 50 µJ from figure 3).

Figure 3. Typical signals in a NRP discharge \( p = 5 \text{ bar}, f = 30 \text{ kHz}, V_0 = 20 \text{ kV}, 150 \mu \text{m gap} \). (a) Synchronized voltage (kV), total current, and conduction current (A). (b) Energy (µJ).

Figure 4. Energy fluctuation with an increase of the gap distance from 150 µm to 250 µm in the NRP discharge. Conditions: pressure \( p = 5 \text{ bar}, \) discharge frequency \( f = 30 \text{ kHz}, \) pulse voltage \( V_0 = 30 \text{ kV}, \) average deposited energy per pulse \( E = 935 \pm 10 \mu \text{J} \).

The pulse energy can be adjusted by varying the pulse voltage \( V_0 \), as increasing the voltage increases the discharge current. Since the breakdown voltage increases with pressure, the minimum pulse energy needed for breakdown also increases. The pressure-dependent breakdown voltage has been measured up to 60 bar and compared with theoretical calculations (provided in appendix C). If the pressure is too high, a fast ablation of the electrodes will occur within a few cycles, hence the plasma cannot be sustained. With the electrodes designed for this study, stable discharges lasting sufficiently long to acquire good conversion data were obtained to pressures as high as 12 bar.

3. Nanosecond pulsed discharge model for plasma-assisted high-pressure CO\(_2\) dissociation

A nanosecond pulsed discharge model is developed to better understand the reaction kinetics of plasma-assisted high-pressure CO\(_2\) dissociation. This zero-dimensional model calculates the time evolution of the temperature and densities of a variety of species in a constant volume, where all plasma parameters are assumed to be spatially homogeneous. The governing equation for species number density \( N_i \) and gas temperature \( T \) is written as

\[
\frac{dN_i}{dr} = \sum_{j=1}^{i_{\text{max}}} \omega_{ij}(r) \quad (i = 1, 2, 3, \ldots, i_{\text{max}}) \tag{1}
\]

\[
\rho c_p \frac{dT}{dr} = q_{\text{coupled}}v_{\text{rep}} - \frac{3}{2} \frac{d}{dr} E_{\text{dis}} - \sum_{i} \epsilon_i \frac{dN_i}{dr} - Q_{\text{loss}} \tag{2}
\]

where \( i \) is the species index in the chemical mechanism and \( N_i \) is the number density of species \( i \). Here, \( \omega_{ij} \) describes the production or consumption rate of species \( i \) contributed by reaction \( j \). The indices \( i_{\text{max}} \) and \( j_{\text{max}} \) are the total numbers of species and reactions considered in the chemical mechanism. In
equation (2), \( \rho \) is the gas density, \( c_v(T) \) is the specific heat, \( q_{\text{coupled}} \) is the coupled pulse energy, \( \nu_{\text{rep}} \) is the pulse repetition rate. \( \Delta E \) is the Boltzmann constant, \( T_e \) is the effective electron temperature, and \( e_i \) represent the internal energy of the \( i \)-th species. \( Q_{\text{loss}} \) accounts for estimated losses from convection or diffusion.

In the zero-dimensional form, the initial electric field \( E_{\text{gap}} \) is computed from the applied voltage \( V_{\text{app}} \) by

\[
E_{\text{gap}} = \frac{V_{\text{app}}}{d}. \tag{3}
\]

The electric field enhancement due to the pin-to-plane geometry was neglected as this would require a multi-dimensional model that is beyond this work’s scope. In our studies, given the gap distance (150–250 \( \mu \)m, see discussions in section 2.1), pressures (5–12 bar), and peak voltage (20–30 kV), the initial reduced electric field \( E/N \) is in the range 660–1100 Td, which is 4–6 times higher than previous atmospheric NRP CO2 dissociation experiments. For example, in the studies of Bak et al [31], the pressure ranges from 2.3 to 5 bar, with a voltage of 9 kV when breakdown occurs, and a gap distance of 0.7 mm. This yields an initial reduced electric field of 105–230 Td. After the breakdown, the high reduced electric field \( E/N \) decays quickly as the current increases.

The input to the numerical model includes species/temperature initial conditions, voltage waveform, and a reaction mechanism. We use a code initially developed at Princeton [33–36] for the numerical solution of the model equations (equations (1)–(3)). It incorporates the plasma kinetics solver ZDPlasKin [37] and the combustion kinetics solver, CHEMKIN II [38], with a splitting scheme. The electron energy distribution function and the rate coefficients of electron-impact reactions are calculated at every time step using the Boltzmann equation library provided by BOLSIG+ [39].

### 3.1. Description of chemical reaction mechanism

The reaction mechanism used in this work consists of 48 species, seven reversible elementary reactions for neutral species, and 614 plasma reactions. It is developed based on the recently validated CO2 mechanisms [40, 41]. All species considered in the model are summarized in table 1. It includes a simplified set of CO2 vibrational levels, in both symmetric modes (CO2(va)-CO2(vd)) [40] and asymmetric modes (CO2(v1)-CO2(v9)) with energy levels from the ground state to 2.5 eV (CO2(v9)). We also consider an extended set of vibrational levels of CO and O2, and electronically excited oxygen species, which accounted for the fast gas heating (FGH) in NRP discharges [28, 42]. Kinetics of CO and CO2 electronic states are simplified and considered as quenching for heat or dissociation. Kinetics of simple ions (such as O\(^+\) or CO\(^{+}\)) and large oxygen ions (such as O\(^{+}\) or O\(^{+}\)) are also included. Clustered ions of carbon oxides, such as C\(_2\)O\(^{+}\) or CO\(^{+}\), are neglected as most reference data has rarely been experimentally validated.

Table 1 presents the different types of reactions included in the mechanism. For electron-impact reactions, the cross-sections for CO2 and CO are obtained from Phelps [43] while those of O2 are from the IST-LISBON database [44] in the LXCat Project [45]. These are added to the BOLSIG+ library. In total, 59 electron-impact processes are considered. Based on the electron-impact cross-section data, the fraction of the electron energy lost to the different degrees of freedom in CO\(_2\)/CO/O2 mixtures are calculated and shown in figure 5. For the pure CO\(_2\) gas, in our setup, the initial reduced electric field is in the range of 660–1100 Td, where the majority of electron energy is invested in electronic excitation and ionization of CO\(_2\). In the presence of the product gas, a considerable amount of electron energy (~20%) is deposited into the electronic excitation of CO and O2, which leads to CO/O2 dissociation and the generation of atomic oxygen species such as O and O\(^{1}\)(D). This redistribution of the electron energy during the CO2 dissociation process has a great impact on the yield and energy efficiency of the overall CO2 splitting process.

To consider the effects of vibrationally excited species on the high-pressure CO2 dissociation, vibrational energy exchange and vibrationally-enhanced chemical reactions are included. For vibrational energy exchange reactions, the vibrational energy is either lost to translational degrees of freedom (V-T relaxation) or exchanged among one or two modes of vibrations (V-V exchange). For the lowest vibrational levels included in the model, we use rate constants available in the literature (including their temperature dependencies) [46, 47]. For the higher levels, we scale these rate constants using a scaling law based on the Schwartz–Slawsky–Herzfeld theory [48]. For vibrationally-enhanced chemical reactions, the products are assumed to be the same as those of the ground-state reactions. However, the vibrational energy can reduce the

### Table 1. Summary of all species included in the model.

| Species type                  | Neutrals and radicals | Vibrationally excited states | Electronically excited states | Positive ions | Negative ions |
|-------------------------------|-----------------------|-----------------------------|--------------------------------|---------------|---------------|
|                               | O, O\(_2\), O\(_1\), C, CO, CO\(_2\) | CO\(_2\)(va), CO\(_2\)(vb), CO\(_2\)(vc), CO\(_2\)(vd), CO\(_2\)(v1), CO\(_2\)(v2), CO\(_2\)(v3), ... CO\(_2\)(v9), CO(v1), CO(v2), CO(v3), ... CO(v10), O\(_2\)(v1), O\(_2\)(v2), O\(_2\)(v3), O\(_2\)(v4) | O\(_2\)(a\(_1\)), O\(_2\)(b\(_1\)), O\(_2\)(^1\text{D}), O\(_2\)(^1\text{S}) | O\(_{+}\), C\(_{+}\), O\(_{2+}\), O\(_{3+}\), CO\(_{+}\), CO\(_{2+}\) | O\(_{−}\), O\(_{2−}\), O\(_{3−}\) |
Table 2. Summary of key reactions in high-pressure CO₂ dissociation. \( (T_r) \) is electron temperature in K. The complete mechanism used in this work is provided in the supplementary material. Gas constant \( R = 1.987 \text{ cal mol}^{-1}\text{K}^{-1} \).

| Reaction | Rate constants, \( \text{cm}^3 \text{s}^{-1} \) or \( \text{cm}^6 \text{s}^{-1} \) | Reference |
|----------|-----------------------------|-----------|
| I. Electron-impact reactions described by collision cross sections | | |
| \( 1 \, \text{e} + \text{CO}_2 \rightarrow \text{e} + \text{CO}_2(v) \) | \( k = f(E/N) \) | [43] |
| \( 2 \, \text{e} + \text{CO}_2 \rightarrow \text{e} + \text{CO} + \text{O} \) | \( k = f(E/N) \) | [43] |
| \( 3 \, \text{e} + \text{CO}_2 \rightarrow \text{e} + \text{e} + \text{CO}_2^- \) | \( k = f(E/N) \) | [43] |
| \( 4 \, \text{e} + \text{CO}_2 \rightarrow \text{CO} + \text{O}^- \) | \( k = f(E/N) \) | [43] |
| \( 5 \, \text{e} + \text{CO} \rightarrow \text{e} + \text{C} + \text{O} \) | \( k = f(E/N) \) | [43] |
| \( 6 \, \text{e} + \text{O}_2 \rightarrow \text{e} + \text{O} + \text{O}(\text{D}) \) | \( k = f(E/N) \) | [43] |
| II. Ion-neutral and ion-ion reactions | | |
| \( 1 \, \text{e} + \text{CO}_2^+ \rightarrow \text{CO} + \text{O} \) | \( 3.8 \times 10^{-7} \times (300/T_r)^{0.5} \) | [50] |
| \( 2 \, \text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO} \) | \( 9.4 \times 10^{-10} \) | [51] |
| \( 3 \, \text{CO}^+ + \text{O} \rightarrow \text{O}_2 + \text{CO} \) | \( 1.4 \times 10^{-10} \) | [52] |
| \( 4 \, \text{O}^+ + \text{CO} \rightarrow \text{CO}_2 + \text{e} \) | \( 6.49 \times 10^{-10} \) | [53] |
| III. Vibrational energy transfer reactions | | |
| \( 1 \, \text{CO}(v) + \text{M} \rightarrow \text{CO}(v-1) + \text{M} \) | \( k = f(v, M, T_{\text{gas}})^a \) | [40, 48, 54] |
| \( 2 \, \text{CO}(v = n) + \text{CO}(v = m) \rightarrow \text{CO}(v = n-1) + \text{CO}(v = m+1) \) | \( k = f(n, m, T_{\text{gas}})^a \) | [40, 48, 54] |
| \( 3 \, \text{CO}_2(v) + \text{O} \rightarrow \text{CO} + \text{O}_2 \) | \( 1.06 \times 10^{-3} T_{\text{gas}}^{-0.45} \exp((E_a - \alpha E_v)/T_{\text{gas}}) \) | [47] |
| \( 4 \, \text{CO}(v) + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} \) | \( 2.09 \times 10^{-11} \exp((E_a - \alpha E_v)/T_{\text{gas}}) \) | [47] |
| IV. Electronic energy transfer reactions | | |
| \( 1 \, \text{O}(\text{D}) + \text{CO}_2 \rightarrow \text{CO} + \text{O}_2 \) | \( 2.09 \times 10^{-10} \) | [55] |
| \( 2 \, \text{O}(\text{D}) + \text{CO}_2 \rightarrow \text{CO}_2 \) | \( 8.01 \times 10^{-11} \) | [56] |
| \( 3 \, \text{O}(\text{D}) + \text{O}_2 \rightarrow \text{O} + \text{O}_2(b1) \) | \( 2.6 \times 10^{-11} \exp(67.0/T_{\text{gas}}) \) | [48] |
| V. Reversible elementary reactions | | |
| \( 1 \, \text{CO} + \text{O} + \text{M} \leftrightarrow \text{CO}_2 + \text{M}^b \) | \( k_0 = 1.70 \times 10^{-33} \exp(3001/RT_{\text{gas}}) \) | [57] |
| \( k_\infty = 4.97 \times 10^{-28} \exp(2380/RT_{\text{gas}}) \) | | |
| \( 2 \, \text{CO} + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{O} \) | \( 2.09 \times 10^{-11} \exp(4.07 \times 10^4 R/T_{\text{gas}}) \) | [58] |
| \( 3 \, \text{O} + \text{O} + \text{M} \leftrightarrow \text{O}_2 + \text{M} \) | \( 1.70 \times 10^{-32} T_{\text{gas}}^{-0.5} \) | [57] |

*a Different kinds of vibrational energy transfer reactions are modeled following different methods. The rate constants may depend on the vibrational level \( v \), collision partner \( M \), gas temperature \( T_{\text{gas}} \), activation energy \( E_a \), efficiency \( \alpha \), and vibrational energy \( E_v \), as discussed in section 3.1.

*b This reaction is treated using the Lindemann formula. \( k_\infty \) and \( k_0 \) refer to high and low pressure limit rate constants.

Figure 5. Electron energy loss fractions for different internal degrees of freedom in this work for two mixtures: pure CO₂ and CO₂/CO/O₂ = 70:20:10.

activation energy barrier of the reaction and thus increase the reaction rate constant. The Fridman–Macheret \( \alpha \)-model [47] is used to consider this type of reaction. For simplicity, electron-impact de-excitation, and electron-impact excitation of excited states are neglected in this model.

As shown in figure 6, the energy deposited at given conditions matches reasonably well with the experimental measurements. The modeled gas temperature profile for one pulse is also provided. The peak temperature reaches \( \sim 3000 \text{ K} \) due to intensive energy transfer processes in the plasma and then decays to the ambient temperature within tens of microseconds. The order of magnitude for the temperature rise is consistent with previous experimental measurements of gas temperatures in atmospheric NRP discharges such as [26, 49]. The peak reduced field \( E/N \) in the modeling is in the range of 660–1100 Td. The initial electron number density is set to \( 10^{10} \text{ cm}^{-3} \) while the peak electron number density in the discharge phase is on the order of \( 10^{17} \text{ cm}^{-3} \).

3.2. Connections between experiments and zero-dimensional kinetic modeling

Given the fact that this work includes a variety of time scales ranging from nanoseconds to minutes, the purpose of zero-dimensional kinetic modeling is not to replicate the exact
experimental results but to identify important kinetic pathways under high pressure conditions. We simplify the kinetic modeling based on the following arguments described in the next paragraph.

As shown in figure 7, the experiments were performed at a time scale of minutes, i.e. $O(10^2 \text{s})$, while the pulse width of every NRP pulse lasted for tens of nanoseconds, i.e. $O(10^{-8} \text{s})$. During the inter-pulse period, which is of $O(10^{-5} \text{s})$, plasma-generated species such as radicals, excited species or electrons/ions, will either recombine, relax, or quench. The temperature in the gap will return to the initial temperature. Therefore, we assume that by the time of arrival of the next NRP pulse, only major components such as CO$_2$, CO and O$_2$ remain. Other by-products and unstable species cannot accumulate beyond one pulse. The temperature will return to the initial temperature. Such a hypothesis is further supported by GC measurements and modeling as discussed in section 4.1.

Based on the above analysis, it is convenient to decompose minute-long processing times into multiple single NRP pulses with different initial CO$_2$/CO/O$_2$ concentrations. Such a strategy can greatly reduce the computational burden and determine the steady-state CO$_2$ yield. The equilibrium condition is satisfied when CO$_2$/CO/O$_2$ concentrations remain constant within a new pulse.

4. Results and discussions

To facilitate the following discussions, we first define energy efficiency $\eta$, conversion degree $\Phi$, and the specific energy input (SEI).

The conversion energy efficiency for CO$_2$ dissociation is defined as [47]:

$$\eta = \frac{\Delta H}{E_{CO}}. \quad (4)$$

Here, $\Delta H$ is the enthalpy of the CO$_2$ dissociation reaction:

$$\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2, \quad \Delta H = 2.9 \text{ eV} \quad (5)$$

and $E_{CO} = E_{\text{tot}}/N_{CO}$ is the average energy required for each CO molecule that is produced, the total number of which is $N_{CO}$. The total energy deposited in any single experiment, $E_{\text{tot}}$ is given as

$$E_{\text{tot}} = E_{\text{pulse}} \cdot f \cdot \tau \quad (6)$$

i.e. it is the product of the pulse frequency, $f$, the processing time, $\tau$, and the energy deposited per pulse, $E_{\text{pulse}} = \int_{\text{pulse}} V(t)dt$. In our experiments, the frequency is held constant at 30 kHz,
Figure 8. Effects of processing time on the CO$_2$ conversion degree and energy efficiency at experimental conditions as pressure $p = 5$ bar, initial temperature $T_0 = 300$ K, initial X$_{CO_2} = 1$, discharge frequency $f = 30$ kHz.

The processing time varies from 30 s to 1500 s, and $E_{\text{pulse}}$ varies from 300 $\mu$J to 1 mJ.

The total number of CO molecules produced, $N_{CO}$, is derived from the gas chromatographic measurements. Appendix B describes the relationship between the number of molecules and the GC signals, taking into account compressibility correction and the effect of the presence of other residual molecules not detected by the GC. The conversion efficiency, $\Phi$, is defined as the ratio of the number of CO molecules produced to the initial number of CO$_2$ molecules in the reactor, $N_0$:

$$\Phi = \frac{N_{CO}}{N_0}.$$  \hfill (7)

In the literature, the conversion degree is sometimes referred to as the (molecular) conversion efficiency [11]. In appendix B, it is shown that the conversion degree is expressed as $\Phi = \chi_{CO}/(\chi_{CO} + \chi_{CO_2})$ where the mole fractions of CO and CO$_2$ ($\chi_{CO}$ and $\chi_{CO_2}$, respectively) are a direct output of the GC measurements. The initial number of CO$_2$ molecules, $N_0$, is calculated from the initial pressure and temperature in the chamber ($P_0$ and $T_0$), the chamber volume, $V$, and the CO$_2$ compressibility, $Z(P, T_0)$ [11]. The number of CO molecules produced is then:

$$N_{CO} = \frac{\chi_{CO}}{\chi_{CO} + \chi_{CO_2}} \cdot \frac{P_0 V}{Z(P, T_0) RT}.$$  \hfill (8)

The energy efficiency, as defined in equation (4), can be calculated from equations (5) and (7). For this purpose, it is useful to introduce the SEI:

$$\text{SEI} = \frac{E_{\text{tot}}}{N_0}.$$  \hfill (9)

The SEI corresponds to the mean energy used per CO$_2$ molecule that was present initially in the batch reactor, or the inlet flow for the case of a flowing system. The SEI is a parameter that allows us to compare different plasma dissociation techniques. Three parameters are related via:

$$\eta = \frac{\Delta H \cdot \Phi}{\text{SEI}}.$$  \hfill (10)

4.1. Time dynamics of NRP CO$_2$ conversion

Experiments were first performed to explore the time dynamics of CO$_2$ conversion degree and energy efficiency, as shown in figure 8. The measurements were not carried out in any particular order (in terms of processing time) to prevent any systematic bias associated with potential electrode erosion.

From figure 8(a), during the initial processing time (to the point where the conversion degree reaches about 10%), the conversion degree increases almost linearly with time. Beyond this initial period, the onset of saturation was observed and the maximum CO$_2$ conversion is 18%. This saturation is attributed to reactions that destroy the formed CO. In all conditions studied, GC measurements confirmed that $N_{CO} \sim 2N_{O_2}$. In other words, over long processing times, no other products of CO$_2$ splitting were formed in significant numbers. Particularly, additional oxygen compounds, such as O$_3$ [15], were negligible compared to the estimated uncertainty of the measurements.

Figure 8(b) provides additional measurements for conversion degree and energy efficiency within the initial processing stage. Within 400 s, the CO$_2$ conversion degree increases linearly with the processing time while the energy efficiency slightly drifts from 27% to 22%. From figure 8(b), to maximize energy efficiency, experiments should be carried out in the initial non-saturated stage, where the conversion degree remains low. Such findings not only emphasize the importance of the CO/CO$_2$ separation technologies, but indicate that kinetic interactions among CO$_2$, CO, and O$_2$, on the time scale
from nanoseconds to minutes, are critical for the efficiency, as discussed in the next paragraph.

Within one pulse, a three-stage kinetic model is presented for the CO\(_2\) dissociation. It is based on the species profiles, and reaction rates for CO’s dominant reactions (as shown in figure 9), together with a reaction path flux analysis.

- Stage I spans the initial NRP discharge phase of several nanoseconds. It is the most energy-intensive stage and electron-impact kinetics dominate over this period. Ground and excited states of CO are formed promptly due to the reactions with energetic electrons. The dominant CO formation pathway is electron-impact dissociation of CO\(_2\):\[e + \text{CO}_2 \rightarrow e + \text{CO} + \text{O} \quad (R_1)\]
\[e + \text{CO}_2 \rightarrow e + \text{CO} + (\text{1D}) \quad (R_2)\]
Secondary CO formation pathways include quenching of O(1\text{D}) or recombination of CO\(_2^+\), i.e.
\[\text{O} \quad (\text{1D}) + \text{CO}_2 \rightarrow \text{CO} + \text{O}_2 \quad (R_3)\]
\[e + \text{CO}_2^+ \rightarrow \text{CO} + \text{O} \quad (R_4)\]

Note that O(1\text{D}) or CO\(_2^+\) are both from electron-impact reactions such as \[e + \text{O}_2 \rightarrow \text{O} + \text{O} \quad (\text{1D}) \quad (R_5)\]
\[e + \text{CO}_2 \rightarrow e + e + \text{CO}_2^+ \quad (R_6)\]
and (R\(_2\)) shown above. During this stage, a portion of the ground state CO\(_2\) or CO is pumped into higher vibrational states, causing the ground state CO to decrease after 2 ns (as shown in figure 9(a)). However, this vibrational ladder mechanism does not essentially change the ultimate CO yield as most of the excited states will be converted back to the ground state in the next stage.

- Stage II spans the period from tens to hundreds of nanoseconds. The major kinetics in this period is the V-T relaxation: excited states are quenched to the ground state, for example,
\[\text{CO} \quad (v = n) + \text{CO} \quad (v = m) \rightarrow \text{CO} \quad (v = n - 1) + \text{CO} \quad (v = m + 1) \quad (R_8)\]

In stage II, the increase in the ground state CO is not directly from CO\(_2\), but excited states of CO. Some vibrationally-enhanced chemical reactions are considered and influence the CO yield, for example,
\[\text{CO} \quad (v) + \text{O} \rightarrow \text{CO}_2 + \text{O} \quad (R_9)\]
\[\text{CO} \quad (v) + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} \quad (R_{10})\]

Nonetheless, their reaction rates are several orders slower than the V-T relaxation. Also at this stage, a significant temperature increase has been captured by the kinetic model (see figure 6), consistent with discussions seen in previous work [28]. At the end of this stage, the concentration of plasma-generated species such as ions, and excited species is below 1 ppm.

- Stage III spans from 0.1\(\mu\)s to the beginning of the next pulse. It is controlled by neutral elementary kinetics. Reversible reactions such as
\[\text{CO} + \text{O} + \text{M} \leftrightarrow \text{CO}_2 + \text{M} \quad (R_{11})\]
are the major reactions determining the CO yield. At this stage, no more energy from plasma is deposited but chemical equilibrium can be shifted by varying the thermodynamic conditions. For example, as pressures are increased from 5 to 12 bar, three-body reaction \((R_{11})\) is approaching its high-pressure limit. More CO is converted back to CO\(_2\) at high pressures from this pathway, which causes a decrease in CO\(_2\) dissociation efficiency as discussed in section 4.2.

The above three-stage model provides a general description for CO\(_2\) dissociation in individual pulses. However, the experimental measurements for CO\(_2\) conversion were not fulfilled within one or two NRP pulses, but rather thousands of pulses over the minute-long processing time. Next, we explore the long-time-scale CO\(_2\) dissociation by decomposing it into single NRP pulses with different initial CO\(_2\)/CO/O\(_2\) ratios (see justification in section 3.2).

Figure 10 shows the predicted CO yield after one NRP pulse with different initial CO/O\(_2\)/CO\(_2\) concentrations, where below 10%, CO yield follows a linear increase, and beyond 10%, a non-linear saturation stage is observed, consistent with the experiment (see figure 8). From the path flux analysis, with an increasing concentration of CO and O\(_2\), the ratio of the CO consumption flux over its formation flux is larger, leading to a smaller increment of the CO yield. More CO and O\(_2\) are present meaning that more electron energy flows into their internal energy states, such as electron-impact dissociation channels \((R_3)\). Such energy redistribution provides more

\[
\text{CO}_2 + O \leftrightarrow \text{CO} + O_2 \quad (R_{12})
\]

atomic oxygen. As a result, kinetics in Stage III are influenced. For example, \((R_{11})\) forward reaction rates are increased, converting CO back to CO\(_2\) and resulting in a decrease in the CO yield. The elementary kinetics of \((R_{11})\) has been well-discussed by [57]. The uncertainty factor is 2–3 from room temperature to 3000 K, which leads to an uncertainty of 6% on the predicted CO\(_2\) conversion and 10% on the predicted energy efficiency.

The equilibrium CO conversion yield from pure kinetic modeling is 32 ± 6%, and different from the measured equilibrium CO yield \((18 ± 5\%)\) by a factor of 1.8. Clearly, other effects are affecting the yield. For example, one key factor which is neglected in the current zero-dimensional modeling is species transport into/out of the discharge/reaction region. In CO\(_2\)/CO/O\(_2\) mixtures, the mixture-averaged transport coefficient of CO\(_2\) is calculated to be 0.05–0.25 cm\(^2\) s\(^{-1}\) at the experimental conditions (5–12 bar), given that the spatial scale of the discharge is approximately 150 µm, the diffusion time scale can be estimated to be

\[
\tau_D = \left( \frac{D}{L^2} \right)^{-1} \quad (11)
\]

which is on the order of 10\(^{-3}\) s. Adding a straightforward estimation of the diffusion term as

\[
Q_D = \frac{N_i - N_i^0}{\tau_D} \quad (12)
\]

to the governing equation (1) leads to a shift of the CO\(_2\) conversion yield, as shown in figure 10. Flow and transport effects in high-pressure NRP discharges are known to be more complicated [59–61]. A careful discussion of the coupling between transport and kinetics requires multi-dimensional numerical modeling [62, 63], which is beyond the scope of this work.

Summarizing this section, we find that high-pressure CO\(_2\) conversion exhibits non-linear time dynamics. From the experiment, the conversion degree saturates beyond a certain processing time while the energy efficiency monotonically decreases with time. From the modeling, within one pulse, the CO number density presents a three-stage time dynamics, controlled by electron impact kinetics, V-T relaxation, and pressure-dependent elementary kinetics. With the accumulation of pulses, the electron energy is re-distributed towards CO and O\(_2\). Three-body CO recombination to CO\(_2\) is facilitated, which leads to efficiency degradation. Other factors such as transport can be critical in determining the final CO yield.

4.2. Effects of pressure

Limited studies have examined NRP CO\(_2\) dissociation beyond 1 atm. How pressure shifts the NRP CO\(_2\) yield and efficiency needs further investigation.

We first fixed the average energy to 640 µJ and measured CO\(_2\) conversion degree and energy efficiency from 3.5 bar to 12.2 bar, as shown in figure 11(a). It is found that within 400 s, the conversion degree decreases inversely with pressure, dropping from 8% to 2%, while the energy efficiency is insensitive.
to pressure, at around 20%. Based on equations (4) and (6), the insensitivity indicates that under different pressures, the number density of CO is mostly dependent on the deposited energy.

The output from kinetic modeling, as shown in figure 11(b), provides a qualitatively consistent trend for the conversion degree $\Phi$ in comparison with the experiment. The quantitative agreement is not expected because the experimental data is collected after a plasma processing time of 400 s based on the whole reactor volume, while the modeling is made after only one NRP pulse inside the discharge volume. With the increase of pressure, gas number density $N$ increases, $E/N$ decreases, and more electron energy is invested in rotational/vibrational excitation rather than electronic excitation or ionization. The electron number density and the electron energy both decrease at high pressures. In the after-glow phase, the atomic oxygen is quickly quenched, controlled by the three-body recombination reactions, primarily

$$O + O + M \rightarrow O_2 + M.$$  \quad (R_{13})

With less atomic oxygen, the chemical equilibrium of reaction (R_{12}) as

$$CO_2 + O \leftrightarrow CO + O_2$$

is shifted backwards and more CO is converted back to CO$_2$. As a result, at higher pressures, the rise in CO number density is not proportional to the rise in total number density.

The prediction of the energy efficiency dependency on the pressure, however, deviates from the experiment. It indicates that other mechanisms exist for CO losses at high pressures. One possible mechanism is product species diffusion which we discussed in section 4.1. Our simple estimate may be under-predicting the diffusion rate, as also suggested by the over-prediction of the saturated yields. At higher pressures, the mean free path is reduced, and the diffusion time scale is increased. The generated CO requires a longer time to be transported out of the discharge volume to avoid plasma-assisted dissociation or chemical conversion. Considering the predictions based on kinetic modeling, the actual energy efficiency will be degraded at higher pressures due to the slower diffusion. Better mixing strategies should be implemented for future high-pressure CO$_2$ conversions.

It is also worth noting that the pressure inside the plasma kernel may exceed the threshold pressure ($P_c = 73.8$ bar) for supercritical conditions, as shown in figure 12. Previous studies of supercritical plasma discharges for material synthesis applications have been reported [64]. The plasma chemistry of supercritical CO$_2$ conversion is poorly understood. We have
performed preliminary molecular orbital calculations using MOPAC\cite{65}. They suggest that under extreme pressures, oxygen constituents of CO\(_2\) are at such proximity that the C–O vibrational bond is sufficiently active, the kinetic barrier to the direct dissociation pathway:

\[ e + \text{CO}_2 \rightarrow e + \text{CO} + \frac{1}{2} \text{O}_2 \quad (R_{14}) \]

may be substantially reduced. Supercritical plasmas are promising for CO\(_2\) dissociation kinetics as \((R_{14})\) will bypass atomic oxygen kinetics such as \((R_1)\) and \((R_2)\) and avoid three-body recombination \((R_{11})\) that converts CO back to CO\(_2\). Nonetheless, with more molecular oxygen present, the chemical equilibrium of the oxygen recycling reaction \((R_{12})\) will also shift and influence the CO\(_2\) yield. Future experimental and theoretical studies are both needed for understanding CO\(_2\) splitting assisted by supercritical plasmas.

4.3. Effects of energy deposition

To understand how the conversion is affected by the deposited energy, we have varied the energy at a given pressure by adjusting the voltage or the gap distance. With varying peak voltage or gap distance, the maximum reduced field \(E/N\) is changed, which leads to different plasma kinetics and an overall different conversion yield and energy efficiency. As shown in figure 13(a), the conversion degree \(\Phi\) increases linearly with pulse energy whereas the energy efficiency \(\eta\) slightly increases, from 16 to 24%. The measurement supports the analysis from section 4.1: vibrational excitation is not the only mechanism at play for CO\(_2\) dissociation. If that is the case, decreasing the peak voltage and energy deposition, in other words, decreasing the reduced electric field \(E/N\) would yield higher efficiencies as more of the electron energy would be used to excite vibrational modes. However, the opposite trend was observed.

From the kinetic modeling, with an increasing peak voltage from 16.2 kV to 28.4 kV, the peak reduced field \(E/N\) in one NRP pulse is increased from 440 to 740 Td, and the energy deposition is from 110 \(\mu J\) to 741 \(\mu J\). A comparison of the reaction rates of electron-impact vibrational excitation, dissociation, and ionization is shown in figure 13(b). With higher \(E/N\) and energy deposition, the rates for electron impact kinetics are all enhanced. However, the rates of electron impact vibrational reaction of CO\(_2\) is enhanced by 19%, while those of electronic excitation and ionization are increased by 28% and 37%. By controlling the electron energy fraction at different \(E/Ns\), it is possible to increase the CO\(_2\) conversion degree while maintaining good energy efficiency.

4.4. Results in context of prior work

The experiments were performed for a broad range of pressures (5–12 bar), pulse energies (300–700 \(\mu J\)), and processing times (40–420 s). In all cases, the energy efficiency is close to \(\eta \approx 20\%\). The slight departure from this value comes from the non-linear dependency on the pulse energy as discussed in section 4.3. The highest energy efficiency is \(\eta = 27\%\) and is obtained with a conversion rate of \(\Phi = 4\%\) for the following conditions: \(p = 5\ \text{bar}, E_{\text{pulse}} = 865 \pm 100 \mu J, \tau = 420\ \text{s}\). The highest conversion rate is \(\Phi = 14\%\) and is obtained with an energy efficiency of \(\eta = 23\%\) for the following conditions: \(p = 5.8\ \text{bar}, E_{\text{pulse}} = 700 \pm 75 \mu J, \tau = 420\ \text{s}\).

These results confirm that the SEI is the critical parameter that determines the conversion degree of the discharge. Figure 14 gives a summary comparison of our results with other work from the literature. It depicts the relationship between the conversion degree, energy efficiency, and the SEI for our experiments, as well as for different plasma dissociation techniques, such as DBD, packed-bed DBD, gliding arc, MW, RF, and other NRP discharges. Isoefficiency lines are also reported. On the logarithmic graph of conversion degree versus SEI, the energy efficiency is represented by parallel
The conversion degree against specific energy input for different non-thermal plasma techniques: microwaves (MW) [5, 13, 66, 67], nanosecond repetitively pulsed (NRP) discharges [31], dielectric barrier discharges (DBD) [15, 16], packed-bed (PB-DBD) [68], radio-frequency (RF) [8], gliding arc [23]. The diagonal lines are iso-efficiency lines for energy efficiency from 1 to 100%.

Most of the experiments reported on this graph exhibit a relatively low sensitivity of the energy efficiency on the SEI, and in particular on pressure. This finding is important to be able to scale the processes to higher throughputs and increased conversion degrees without reducing efficiency. It seems to apply particularly to some techniques. In DBD discharges, the linear dependence of the conversion degree on the SEI has already been reported by Brehmer et al [15] for a range of density and confirmed by the analysis of Bogaerts et al [68]. On the other hand, low-pressure discharges such as the reported MW experiments are particularly sensitive to pressure conditions as evidenced by the results of Rusanov et al [5] and of Van Rooij et al [66] (although only one pressure is reported on figure 14 for the sake of clarity).

It follows that, although convenient to predict the conversion degree, the SEI is not the only parameter required to characterize the efficiency of a given technique. Experiments carried out with MW discharges by Rooij et al and Silva et al exhibit large disparities in efficiency. Similarly, in the NRP experiments of Bak et al and those of this work, the energy efficiency differs by almost a factor of two (13% to 20% average) despite the same range of SEI investigated. In these studies, the same high-voltage generator is used, hence the same pulse shape and pulse duration. The range in pressure and energy deposited overlap as well. The experiments of Bak et al were performed in a flow reactor, possibly reducing the processing time of a fluid element to the plasma (note that figure 8 shows that a reduced processing time has a small but positive effect on the energy efficiency).

5. Conclusion

In this work, CO₂ dissociation at high pressures using NRP discharges has been investigated from both an experimental and a numerical standpoint. In a batch reactor configuration, the experiments were performed for a broad range of pressures (5–12 bar), pulse energies (300–700 µJ), and processing times (40–1200 s). A zero-dimensional kinetic model for plasma-assisted high-pressure CO₂ dissociation is also developed and validated in this work. First, the measured byproducts of CO₂ conversion exhibit nonlinear time dynamics. The conversion degree is saturated, and the energy efficiency is decreased with the increasing processing time. Kinetic modeling reveals that the nonlinear time evolution within one pulse is controlled by three-stage kinetics. Electron-impact dissociation, vibrational relaxation, and reversible elementary kinetics dominate over each stage. The saturation of CO₂ conversion over a long processing time is controlled by three-body recombination and possibly species transport effects. Next, the effects of pressure and deposited energy are investigated. For conditions where the conversion degree is less than 15%, the energy efficiency is found to be about 20% and exhibits low sensitivity to the pressure, pulse energy, and residence time conditions. The energy conversion degree can be expressed as a linear function of the SEI. A conversion rate of up to Φ = 14% is achieved with an energy efficiency of η = 23% for the following conditions: P = 5.8 bar, Epulse = 700 ± 75 µJ, τ = 420 s. Kinetic modeling also indicates that beyond 10 bar the CO₂ conversion can enter the supercritical conditions, where the direct dissociation of CO₂ into O₂ is hypothesized. Finally, comparing our results with previous NRP experiments, we find the energy efficiency to be almost twice that of these previous studies. We attributed this finding to the higher electric fields that are used in this work. An examination of the different CO₂ dissociation channels suggests that for high-pressure NRP CO₂ conversion, the electronic excitation is more significant than the vibrational mechanism, which has been discussed extensively in other plasma devices. Future work includes reactor development for plasma-based supercritical CO₂ conversion and first principle calculations for understanding CO₂ kinetics under extreme plasma conditions.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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Appendix A. Electro-chemical etching of the electrodes

In this section, the electrochemical process for electrode fabrication is introduced. It is a variant of the process first developed by Hobara et al [69] for the fabrication of tips used in multi-tip scanning tunneling microscopes. A 2 mm wide tungsten wire is first fastened onto a holder that is connected to a vertical translation pod and then submerged into a solution of sodium hydroxide NaOH (2 mol\(\text{L}^{-1}\)). This submerged wire will serve as an electrochemical anode. The portion of the wire that is not submerged is connected to the positive potential side of a DC (voltage-regulated) power supply. The grounded lead of the power supply is connected to a second electrode that is also submerged into the solution. This second electrode serves as a cathode. The length \((L)\) of the submerged portion influences the radius of curvature of the etched electrode, which is a consequence of the electrochemistry that occurs at the region of the submerged wire near the free surface (described below). We used \(L = 6\ \text{mm}\) to obtain a radius of curvature of 10 \(\mu\text{m}\) when 20 V is applied to the wire. The length of the electrode following the etch process, as subsequently used in the discharge is the non-submerged part of the tungsten wire, and is measured with the vertical translation stage. When installed in the reactor, the electrode gap distance is measured with a precision of approximately 30 \(\mu\text{m}\).

The resulting anodic reactions are described by a six-step mechanism [70]. The global reaction is represented as \(W + 8\text{OH}^- \rightarrow 4\ \text{H}_2\text{O} + \text{WO}_4^{2-} + 6\text{e}^-\), leading to the formation of aqueous tungsten oxide ions and the liberation of tungsten from the surface. The rate of electrochemical etching is faster just below the meniscus, as the convection of OH\(^-\) ions increases the oxidation rate of tungsten [69] (figure A1). As the wire diameter below the meniscus becomes extremely small, the weight of the residual immersed part stretches the tip of the future electrode. Eventually, the lower part is detached under the influence of the combination of anodic oxidation and gravity resulting in a sharp electrode tip. The entire etching process is complete in approximately 20 s. The process results in a consistent taper and tip radius of curvature, as shown by the comparison of ten fabricated samples in the photograph of figure A2.

Appendix B. Analysis of gas chromatographic samples

In this appendix, we discuss the operation of the gas chromatograph and its use for measuring CO and O\(_2\) mole fractions. Two main hypotheses are made in the interpretation of the signals:

- We assume the mixture is inert after the end of the experiment. Successive measurements were carried out with 10 min interval times and no statistically significant change in the chemical composition could be observed, validating this assumption. Chemical reactions inside the GC are also neglected. In particular, we neglect surface CO recombination that may happen in the narrow GC tubing.
- We assume CO and CO\(_2\) are the only two carbon compounds created. The carbon balance equation is then \(N_{\text{CO}} + N_{\text{CO}_2} = N^0\). This assumption is confirmed by our measurements, as
no other C$_1$ or any C$_2$ species are detected, despite the sensitivity of the PDHID detector to all carbon-based compounds.

In extracting samples from the reactor, a mass flow controller is used between the chamber and the GC to maintain a constant flow of 50 cc min $^{-1}$ to the detector. The calibrated GC signal is proportional to the mole fraction of each species. Under (i), the mole fractions in the chamber and in the GC columns are preserved. The molar ratio in the chamber are derived directly from the GC signals. Carbon atom balance results in the following expression for the conversion degree:

$$\Phi = \frac{N_{\text{CO}}}{N^0} = \frac{\lambda_{\text{CO}}}{\lambda_{\text{CO}_2} + \lambda_{\text{CO}}}.$$  \hspace{1cm} (B1)

$N^0$ is determined from the initial chamber pressure, $P_0$, the chamber volume, $V$, and the CO$_2$ compressibility, $Z(P_0)$. The number of CO molecules produced in the reactor is then expressed as:

$$N_{\text{CO}} = \Phi \cdot N^0 = \frac{\chi_{\text{CO}}}{\chi_{\text{CO}_2} + \chi_{\text{CO}}} \cdot \frac{P_0 V}{Z(P_0)RT}.$$  \hspace{1cm} (B2)

It is noteworthy that neglecting CO$_2$ compressibility would significantly underestimate the number of CO molecules created in the chamber. For chamber pressures $P > 10$ bar, this error would be greater than 5%.

Appendix C. Investigation of the pressure-dependent breakdown voltage

This section presents the measurement of the breakdown voltage in the high-pressure facility used in this work within the pressure range of 1 to 60 bar.

It is assumed that the breakdown mechanism in an NRP CO$_2$ discharge is similar to the NRP spark regime observed in atmospheric air [71]. The high repetition rate employed induces a substantial level of pre-ionization electron density for each subsequent pulse. When the pre-ionization electron density surpasses a critical value ($\approx 10^5$ cm$^{-3}$), it prevents the avalanche-to-streamer transition, resulting in the formation of a discharge through Townsend avalanches within the volume. Therefore, in our specific case, the breakdown can be explained by the Townsend mechanism. The experimental outcomes are compared with values estimated by the Paschen theory where the breakdown voltage is obtained by solving the Paschen equation:

$$\gamma (\exp(\alpha d) - 1) = 1.$$  \hspace{1cm} (C1)

where $\alpha$ and $\gamma$ are the first and second Townsend coefficients, and $d$ is the gap distance between electrodes. $\alpha$ is derived from the following semi-empirical equation,

$$\frac{\alpha}{\beta} = A \exp \left( -B \left( \frac{E}{p} \right)^{-1} \right)$$  \hspace{1cm} (C2)

where $A = 20$ cm$^{-1}$ Torr$^{-1}$ and $B = 466$ cm$^{-1}$ Torr$^{-1}$ are taken from the literature [47], $p$ represents the gas pressure, and $E$ denotes the electric field. It is important to note that the Paschen theory is applicable to DC discharges in a plane-to-plane geometry, with the Paschen coefficients typically determined at low pressures. However, at high pressures, a deviation is observed between experimental results and the theoretical predictions in the right branch of the Paschen law. This discrepancy arises due to the influence of ion-enhanced field emissions (IEFEs) occurring at the cathode, as demonstrated by Boyle and Kisliuk [72]. To account for this, we adapt the equations proposed by Muneoka for a high-pressure helium discharge [73]. As a result, the second Townsend coefficient $\gamma$ is expressed as the sum of two components: $\gamma_p$ representing the usual secondary coefficient due to the Auger neutralization effect, assumed to be independent of pressure, and $\gamma_p$, which arises from IEFE:

$$\gamma_p = K \exp (-D_{\text{FN}}E_A), \quad K = \frac{10 C_{\text{FN}} \beta^2 d}{\epsilon_0 \mu}$$  \hspace{1cm} (C3)

where $C_{\text{FN}}$ and $D_{\text{FN}}$, which are related to the work function of the cathode, are provided by Nottingham et al [74]. The effective electric field on the cathode, denoted as $E_A$, is equal to $\beta E$, where $\beta$ represents the geometric field-enhancement factor associated with the shape of the pin electrode. In our study, we utilize $\beta$ as a fitting parameter to indirectly estimate its value in our system. The parameter $\mu$ represents the ion mobility, which is determined by solving the Boltzmann equation [39]. The resulting Paschen curve is illustrated in figure C1. From the figure, $\beta = 0$ indicates that the electrode configuration corresponds to a plane-to-plane setup. Based on our measurements, the value of $\beta$ for the system ranges from 2 to 4.
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