# Carbon dioxide: A Study into Temperature-dependent Carbon-based Plasma Chemistry

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**Abstract:** This study delves into the underlying temperature-dependent carbon-based plasma chemistry using  $CO_2$  as a model. By combining experiments and 0D chemical kinetic simulations, the study examines the plasma chemistry in more detail as a function of gas temperature. By investigating how the conversion of  $CO_2$  is affected by variables such as gas temperature, discharge power, and reduced electric field, the effects of electron and thermal induced chemistry are examined.

**Keywords:** Non-thermal Plasma, Chemical Kinetics, Carbon dioxide, Temperature Controlled Dielectric Barrier Discharge, 0D Simulation.

# 1. Introduction

Carbon dioxide (CO<sub>2</sub>) plasma is a relatively simple and well-understood system that can be used as a base for more complex C1 plasma systems. In addition, CO2 is both a product as well as an intermediate species during the transformation of carbon-based fuels [1]. It influences not only the rates of the reactions but also the chemical pathways. As such, it is necessary to understand the underlying chemistry of CO2 before we advance into more complex carbon-based systems. The use of plasma in converting CO<sub>2</sub> into valuable chemicals and fuels [2-4] is considered a promising approach for transforming greenhouse gas emissions. The research performed by Capezzuto et al. [5] and in the former U.S.S.R. [6] established the use of non-equilibrium plasma for the dissociation of CO<sub>2</sub> through energetic electron impact excitation, ionization and dissociation reactions.

CO<sub>2</sub> plasma modelling typically involves using computational and experimental techniques to understand and predict their behaviour. Numerical simulations, such as zero-dimensional (0D) kinetic models [7-9] are widely used to model CO<sub>2</sub> plasmas. Analytical models [10,11] based on simplified assumptions, can also provide insight into the underlying physics of the plasma. Laboratory experiments are used to study the behavior of CO2 plasmas under realistic conditions. They measure properties such as the electron and ion temperatures, species densities, and heat and mass transfer. Current state-of-the-art involves combining computational and experimental techniques. Research on Multiphysics models [8,12] take into account the interplay between the different physical phenomena that occur in the plasma, such as plasma chemistry, heat and mass transfer, and electromagnetic fields. Additionally, Machine Learning techniques are being incorporated into the simulation process to improve the accuracy of the models.

Previous studies have explored the feasibility of  $CO_2$  splitting using different plasma sources including the use of Dielectric Barrier Discharge (DBD) reactors at room temperature [13-16]. Most previous works use inert gases such as Ar, He and N<sub>2</sub> as dilutants which have been found to have adverse effects in the plasma chemical kinetics

[17,18]. The objective of our study is to develop a plasma chemical reaction mechanism for the accurate description of pure  $CO_2$  plasma-chemistry in a wide range of gas and electron temperatures of interest for temperature-dependent plasma assisted processes, such as plasma-assisted catalysis, oxidation/reduction and combustion.

### 2. Experimental setup

The experimental setup consists of a coaxial type Temperature Controlled DBD reactor (TCDBD) [3], a gas feed system, a power supply system and an analyzing unit as shown in figure 1.



Fig. 1. Schematic of Experimental Setup.

The reactor is a double walled DBD made out of quartz which consists of two zones, a preheating zone and a plasma discharge zone. The temperature control is achieved using a three-zone furnace capable of temperatures up to 1473 K. The reactor consists of an outer and an inner quartz tube separated from each other by a gap distance of 2 mm. The high voltage (HV) electrode, which is made out of a sheet of stainless steel, is inserted in the inner quartz tube. The ground electrode, made of stainlesssteel wire mesh is wrapped around the outer quartz tube, and has a length of 40 mm. The preheat zone of the reactor is so designed as to have sufficient time for the gas to reach equilibrium with the desired background temperature. The discharge zone is designed to be located in the second zone of the furnace to maintain uniform temperature of the gas during the experiment.

Grade 5 (99.999 %) CO<sub>2</sub> is used in order to minimize impurities in the inlet gas, which could otherwise have adverse effects on the chemical kinetics study. A Gas Chromatograph (GC), with one Flame Ionization Detector (FID) and two Thermal Conductivity detectors (TCD), is used to analyze the products. Nitrogen is added to the output of the reactor to be used as internal standard in the GC measurement. It was not added at the reactor inlet to prevent the production of high energy metastable N<sub>2</sub> states which could alter the chemistry. The total flow rate of CO<sub>2</sub> is fixed at 200 SCCM. The voltage to the HV electrode at 2.5 kHz is supplied as a sinusoidal wave in the kV range. A sampling capacitor is connected in series to the ground electrode to measure the charge in the discharge gap. Using a digital oscilloscope, the voltages at the HV electrode and across the sampling capacitor are measured.

Using the charge (Q) and the applied voltage (V), the Lissajous curve [19] (Q-V plot) is mapped. The area under the Lissajous curve gives the discharge power ( $P_{dis}$ ), and the breakdown voltage ( $V_B$ ) is obtained from the plot. Using  $V_B$ , the electric field (E) is calculated and hence the reduced electric field (E/N) is obtained. The experiment was conducted for a gas temperature ( $T_g$ ) of 300–1050 K with an increment of 150 K and  $P_{dis} = 10$  and 20W. E/N,  $P_{dis}$  and  $T_g$  were used as inputs for the numerical simulation and the information on the composition of the products from GC were used to validate the model.

# **3. Numerical Modelling**

In a DBD CO<sub>2</sub> plasma, the main chemical reactions that occur are electronic excitation (including dissociation) and ionization of CO<sub>2</sub> molecules [20,21]. The species that were considered for the modelling are given in table 1.

Tab	ole I	1. Sp	pecies	considered	for	the	numerical	mode	lling.
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Neutrals and Radicals	CO <sub>2</sub> , CO, O <sub>2</sub> , O, C			
Ions	$CO_2^+, CO^+, O_2^+, O^-,$			
CO2 excited species	$\begin{array}{c} (010) \\ (100) \\ (020) \\ (110), (030) \\ (n00), (0n0) & n= sum 4-8 \\ (040), (120), (011) \\ (200) \\ (050), (210), (130), (021), (101) \\ (300) \\ (060), (220), (140) \\ (001) \\ CO_2(^{1}\Pi_g) \\ CO_2(^{1}\Delta_u) \end{array}$			
CO excited species	$\begin{array}{l} \text{Sum of vibrations} \\ \text{CO}(\text{A}^3\Pi) \\ \text{CO}(\text{A}^1\Pi) \\ \text{CO}(\text{A}^3\Sigma) \\ \text{CO}(\text{B}^3\Sigma) \\ \text{CO}(\text{B}^1\Sigma) \\ \text{CO}(\text{C}^1\Sigma) \\ \text{CO}(\text{C}^1\Pi) \end{array}$			
O <sub>2</sub> excited species	$(n_v = 0, n)  n=1-4$ $O_2(A^{1}\Delta_g)$ $O_2(B^{1}\Sigma_g)$ $O_2(A^{3}\Sigma)  O_2(C^{3}\Delta)  O_2(C^{1}\Sigma)$			

A reduced mechanism for CO<sub>2</sub> was developed with the electron impact reactions being referenced from the IST-Lisbon [22] database reported in LXCAT [23]. Five neutral species i.e., ground state molecules and radicals as well as three positive ions and one negative ion are taken into account. GRI Mech served as the base for the thermal chemistry where reactions involving O<sub>2</sub>, CO<sub>2</sub>, CO and O were considered. Simulation using the mechanism with inputs E/N,  $T_g$  and  $P_{dis}$ , obtained from the experiments, was done to validate it. In order to achieve this, an in-house developed 0D plasma-chemical kinetic model named KAUSTKin [24] which couples ZDPlasKin [25] and ChemKin [26] was utilized. A large number of energy pulses were applied in the numerical simulation, which is representative of the residence time of the gas in the discharge zone and the filamentary micro-discharges of the DBD reactor, similar to the works of Snoeckx et al. [24] and Bang et al. [27].

### 4. Results and Discussion

The experiments performed in the temperaturecontrolled DBD reactor yielded a Lissajous diagram. This was used to determine  $V_{\rm B}$  and E/N for various  $T_{\rm g}$  at  $P_{\rm dis}$  = 10 and 20 W. E/N is a significant characteristic of the plasma that affects both the physical and chemical properties and is a crucial input for our 0D model. The trend of E/N is depicted in figure 2. It was found that, when  $P_{\rm dis}$  was kept constant, E/N increased as  $T_{\rm g}$  increased, up to 900 K, but then decreased at 1050 K. The rise in E/N was caused by an increase in  $V_{\rm B}$  and a decrease in the number density of particles (N) as  $T_{\rm g}$  increased. The drop at 1050 K was a result of a significant decrease in  $V_{\rm B}$ , despite the continued decrease in N. As expected, E/N was much higher in 20 W as compared to 10 W.



Fig. 2. Calculated reduced electric field (E/N) from experiments conducted in the TCDBD for  $T_g = 300$  to 1050 K and  $P_{dis} = 10$  and 20 W.

The investigation into the conversion of CO<sub>2</sub> found that the conversion decreased as  $T_g$  increased, regardless of  $P_{dis}$ , as illustrated in figure 3 in symbols. Based on the changes in the energy loss fraction an increase in E/N is expected to result in an increase in ionization and dissociation of CO<sub>2</sub> (as seen in figure 4) and thus increased conversion of CO<sub>2</sub>. However, as we will discuss, the decreasing trend indicates a stronger effect of the thermally induced chemistry/reactions in the studied temperature range. For a given  $T_g$ , the conversion was higher for the higher  $P_{\text{dis}}$ .



Fig. 3. Conversion of CO<sub>2</sub> as a function of  $T_g$  for  $P_{dis} = 10$  and 20 W.

To replicate the standard filamentary behaviour that is typically found in DBDs, where gas molecules move through multiple micro-discharge filaments as they travel, a large number of consecutive micro-discharge pulses were utilized. The conversion of CO<sub>2</sub> obtained from the simulation is shown in Figure 3 with full lines.



Fig. 4. Energy loss fraction as a function of E/N for CO<sub>2</sub>. Reproduced from ref [1] with kind permission; published by The Royal Society of Chemistry

The simulation results were highly consistent with the experimental results. Here again, it was observed that the conversion decreased as  $T_g$  increased. To further understand this phenomenon, the reaction rate constants (*k*) of the most important thermally induced reactions were plotted as a function of  $T_g$  in figure 5. As the temperature increases, the decrease in the reaction rate constant of  $O + O + M \rightarrow O_2 + M$  (R1), combined with an increase in that of  $O + CO + M \rightarrow CO_2 + M$  (R2), leads to an increase in the production of CO<sub>2</sub> through R2, as more of CO is being converted back into CO<sub>2</sub>. This thermal back reaction could

explain the reduction in conversion of CO<sub>2</sub> at higher  $T_g$  despite the increased electron impact ionization and dissociation reactions associated with the increased *E/N*. Even though the reaction rate constant of CO<sub>2</sub> + O  $\rightarrow$  CO + O<sub>2</sub> (R3) exponentially increases with increase in temperature, it is several orders lower in magnitude than R2 and thus has minimal effect.



Fig. 5. Comparison of the reaction rate constants (k) of the most important thermally induced reactions as a function of  $T_{g}$ .

To gain more insight into the impact of  $T_g$ , for higher temperature plasmas (i.e., microwave and gliding arc discharges), numerical simulations were used to study the conversion of CO<sub>2</sub> for temperatures up to 5000 K, in order to distinguish the separate effects of the thermal and electron induced chemistry. The results are shown in figure 6, which compares the conversion of CO<sub>2</sub> under a constant E/N of 200 Td with a  $P_{dis}$  of 20 W, versus a pure thermal case (0 Td).



Fig. 6. Comparison of constant E/N = 200 Td with  $P_{dis} = 20$  W to pure thermal case (0 Td).

The results show that at temperatures up to 2000 K, the conversion of CO<sub>2</sub> is higher when a discharge is present as compared to its absence. This difference in conversion is especially significant for lower  $T_g$  values close to 300 K, indicating that the conversion is due to the discharge (electron impact reactions). When we go from 300 K to 1500 K, we observe the effect of the thermal chemistry leading to a decrease in conversion with increase in  $T_g$ . Hence, for the discharge condition up to  $T_g = 2000$  K, both

electron-induced chemistry and thermal chemistry affect CO<sub>2</sub> conversion. At temperatures above 2000 K, the two plots are similar, indicating that the conversion is solely driven by thermal chemistry and that the electron chemistry has little to no impact on the conversion of CO<sub>2</sub>.

The developed temperature-dependent reaction mechanism for  $CO_2$  can be used at elevated temperatures (300–2000 K) to study plasma assisted catalysis, oxidation/reduction, and combustion processes. Although the current mechanism excludes the v-v transfer process, which is important for MW discharges and can lead to efficient dissociation of  $CO_2$ , the results do indicate that a major portion of the observed conversion for these discharges is mainly governed by the thermal component of the discharge rather than by electron-induced reactions.

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## 6. References

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