DIRECT CURRENT POINT-PLANE CORONA DISCHARGE IN CARBON DIOXIDE

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Abstract

The dissociation of Carbon dioxide in a d.c. point-plane corona discharge reactor is examined at atmospheric pressure to check the efficiency of the device for pollution abatement purposes. The influence of the main parameters of the discharge on the reaction yield is considered.

Keywords: Corona discharge; Carbon dioxide; Atmospheric pressure; Chemical properties; Pollution abatement.

1 Introduction

Among the salient pollutants directly resulting from industrial activity, Carbon dioxide occupies a particular place as the ultimate step for the degradation of organic matter. CO2 is also largely involved in greenhouse effects, which precisely concerns the Earth. Limiting CO2 emissions in the atmosphere is such a fundamental problem that it was scheduled for several international meetings at the highest level and even remains of the hottest topicality. New techniques are tested to limit pollution or to enhance the value of wastes. A NATO Workshop held at Cambridge University (1992) was extended to pollutants other than CO2 and devoted to the non-thermal plasma techniques for pollution control [1]. Two strategies lead to CO2 abatement: the first one aims to limit its production, while the second one intends to transform CO2 into useful and reusable compounds, such as CO. Following the second way, we examine the opportunity presented by a cheap electric technique (i.e., the corona discharge) to transform CO2 to CO.

Dissociation of Carbon dioxide is described as a chemical equilibrium occurring in homogeneous phase:

\[ \text{CO}_2 = \text{CO} + \frac{1}{2} \text{O}_2 \]

It involves an endothermic dissociation reaction (standard enthalpy: \( \Delta H_{298}^\circ = 282.73 \pm 0.12 \text{ kJ mol}^{-1} \)). However, the stability of each species depends on its free energy, additionally to the gas pressure and temperature. CO is then stable at high temperature (i.e., for \( T > 2000 \text{ K} \)), contrary to CO2. The kinetics is obviously related to the thermodynamic stability of the relevant species: CO2 dissociates at high temperature and yields oxygen atoms, which later combine and form oxygen molecules.

Energy may be brought to the CO2 molecules by various methods, among which are electric discharges. A corona type discharge enables the energy transfer from the electric field to the gaseous matter at atmospheric pressure and keeps the macroscopic temperature of the fluid at ambient level. We varied the main discharge parameters (e.g., gas flow rate, \( Q (\text{cm}^3 \cdot \text{min}^{-1}) \), space-time \( t_s (\text{min}) \) of the gas and volume of the reactor), in addition to specific parameters (e.g., polarity of the point electrode, current intensity \( I (\mu\text{A}) \), electrode gap \( d (\text{mm}) \)) to determine their influence on the concentrations of the involved species. The CO2 fractional conversion (FC), referred to as \( X \), was then followed to precise the best conditions for increasing CO.

Several non-thermal plasma studies already deal with the dissociation of CO2 [2-16] in the frame of ozone preparation from CO2 containing air or in connection with lasers. The occurrence of equilibrium was already mentioned and studied by corona type discharges at low pressure [2-4]. A limited number of other papers are also concerned with the corona discharge at atmospheric pressure [5-11]. Some of the most recent ones deal with pulse, arc or barrier discharges [12-14]. In addition, authors concentrate on the influence of the gas flow parameters [5, 9, 15], the gas composition [8-10, 13] or the electrode material [8, 9]. At least, informative data are reported on the dissociation mechanism of CO2 in plasma conditions, and on the relevant kinetic constants for some elementary processes.

2. Experimental technique

The reactor (Fig. 1) is a silica cylinder (inner diameter: 37 mm; length 200 mm) fitted with two 18X10 stainless steel electrodes settled along the
axis of the reactor according to a standard point-to-plane set-up. The point electrode (6 mm in diameter; tip angle 60°) is connected to the positive or negative high voltage. The grounded plane electrode is a disk (30 mm in diameter). The electrode gap (i.e., the distance $d$) may be varied. A generator (Brandenburg Model 380) delivers a constant voltage selected in the range 0-30 kV. The feed gas CO$_2$ (Air Liquide) passes through a flow meter fitted with a needle valve before entering the reactor.

Before use, the reactor is purged of all residual gases, including air, by means of Argon sweep. Then the working gas CO$_2$ is admitted and its flow fixed, as are the electrical and geometrical parameters of the discharge. Gas samples are taken at the reactor output and analysed by GPC. The chromatograph used (Intelsmat 121 ML, fitted with a catharometer as the detector) is equipped with three columns disposed in series. The 1st column is filled with silica gel and raised to 100 °C; it allows separating CO$_2$ from the gas mixture. The 2nd column is a delay column and the 3rd one is filled with 13X molecular sieves and kept at ambient temperature.

![Figure 1: Scheme of the corona reactor; (G: generator; R = 25 MΩ: safety resistance; A microamperemeter; V: kilovoltmeter; S: sampling chamber; Gas: gas inlet and outlet).](image)

The fractional conversion of Carbon dioxide (FCC) is given by $X = 1 - n(CO_2)/n^0(CO_2)$ and involves the initial number $n^0(CO_2)$ of CO$_2$ molecules present in the reactor and the relevant number $n(CO_2)$ at the considered time. X may be related to the output and input CO$_2$ flows assuming that only Carbon mono and dioxide are present as carbonaceous matter. The X values are determined from the peak areas of the chromatograms related to CO$_2$ and CO. $X_{CO}$ is similarly defined as $n(CO)/n^0(CO_2)$.

3. Results
3.1 The Corona Discharge

A Corona discharge [18,19] is a self-sustained discharge, which takes place between two conductors of different shapes (e.g., a point and a plane or a wire and a cylinder) when a high voltage fall, higher than the threshold potential and lower than the breakdown potential, is applied between them. The particular geometry of the point electrode (fitted with a small curvature radius), which is raised to the high voltage, makes that the interactions between the electric energy and the gas give rise to luminous, acoustic and chemical phenomena. These interactions are maximum in the volume where the electric field lines concentrate, that is in the ionisation zone located at the tip of this electrode. The energy transfer to the gas occurs in this zone and modifies the local composition of the phase, so that excited heavy species (i.e., molecules, radicals, atoms and ions) mix with unexcited heavy gaseous species and the plasma gas collectively becomes highly reactive. Ions, molecules, radicals and atoms are present in the ionisation zone, in addition to light species (i.e., electrons and photons). A space charge at the edge of the ionisation zone gathers the charged species of an opposite sign to the point electrode, due to the electrostatic effect. Hence, only heavy chargeless species and ions of the same sign as the point electrode are present in the drift zone between the electrodes. Contrary to the diffusion phenomena observed in solution electrochemistry processes, the transfer of matter follows only one direction: it takes place from the point electrode to the plane electrode, whatever is the discharge polarity and it is known as the electric wind.

3.2 Operating the CO$_2$ reactor

Operating a corona discharge depends on the nature of the gas where the discharge occurs, for given geometrical parameters. The d.c. corona conditions result from three primary parameters: the current intensity, the voltage fall (for a given polarity of the electrodes) and the electrode gap $d$.

Figure 2 illustrates the variations of the current intensity $I$ vs. applied potential $U$, for given $d$ values, for positive and negative discharges. Conventionally, $I$ and $U$ are positive for a positive discharge (the point electrode is raised to the high positive potential) and negative in the other case. The comparison between the plots relevant to a given $d$ value in positive and negative discharges confirms a feature already observed for other gases: a negative discharge allows exploring a larger potential range than a positive discharge. The limit potentials depend on the nature of the plasma gas and of the electrode materials [8, 9]. They are associated with the occurrence of streamers, so that the corona conditions are no
more realised and this feature is related to the electric mechanism of the streamer formation [18, 19].

![Figure 2: Current vs. Potential plots for positive and negative corona discharges in CO₂, for various electrode gaps d (mm).](image)

The electric phenomena, which occur in the discharge, induce two main effects, which are not independent. The first one is the formation of activated species (molecules, ions, radicals and occasionally atoms) as already mentioned. The second one results from using a couple of electrodes: one acts as an anode and the other as the matching cathode. Species may then oxidise at the anode and reduce at the cathode, as they do in usual electrolysis processes. In addition, the electric wind asymmetrically transfers the species formed at the point electrode to the vicinity of the plane electrode. They can then react, either by oxidation-reduction reaction at the electrode surface or with the species already formed at the plane electrode. Thus, electrolysis processes are partly involved in the corona discharge mechanism [20]. This feature explains why the current intensity, which governs the electrolysis reactions, has a basic influence on the chemical effects induced by a corona discharge.

Dissociation of CO₂ corresponds to the decrease in the oxidation state of Carbon from (+IV) to (+II) and to the matching increase in the oxidation state of Oxygen. Since oxidation and reduction processes are closely related to the electron flows, one can guess that the current intensity of the discharge is of major importance for the dissociation process of CO₂ in corona conditions.

A matching argument in favour of this electrochemical approach is relevant to the corona discharge in CO: for very high negative applied voltages, the formation of a carbonaceous thread is observed at the tip of the point electrode. This may be related to the overall reduction of Carbon from the oxidation state (+II) to (0). Similar observations are reported [21] when volatile organic compounds are removed by means of a pulsed dielectric barrier discharge reactor.

Other key parameters govern the dissociation of CO₂. We examined their influence to select the most representative ones. For constant gas pressure (p = 10⁵ Pa) and macroscopic temperature T (in the range 299.5 - 308.5K, since a very small thermal effect is observed [22]), we investigated the influence of several parameters on X.

We first considered primary parameters such as the current intensity, the electrode gap d, the input energy P and the gas flow-rate Q for both positive and negative discharges.

Other useful parameters, such as the plasma energy density P/N, which correlates the input energy P(W) with the number N of gas moles in the reactor, will be derived and discussed as possible key parameters to account for the chemical effects of the discharge. At least we assume to operate in plug flow tubular reactor [16,17], so that the space time t° is the useful time parameter to account for the reactor efficiency.

Although the corona discharge is operated at atmospheric pressure, it is not usually classified among the thermal plasmas for which equilibrium takes place between the electrons and the heavy species. Hence, our standard operating conditions for the discharge are close to non-equilibrium conditions.

![Figure 3: Evolution with the treatment time t (min) of the fractional Carbon dioxide conversion X for various current intensities I (µA) for a negative corona discharge (d = 15 mm; Q = 500 cm³ s⁻¹; p = 10⁵ Pa.)](image)
3.3 Pseudo-equilibrium (or dynamic equilibrium) conditions

In any case, dissociation of CO₂ usually needs high temperatures. The occurrence of this equilibrium in the corona conditions confirms that this type of discharge may be considered as a model for thermal plasmas although the macroscopic temperature remains close to ambient.

3.4 Influence of the current intensity

The delay needed to reach dynamic equilibrium is illustrated in figure 3 in the case of a negative discharge and for various current intensities. For all the series of experiments, equilibrium is reached after 60-min treatment. We have to consider two situations, which are respectively relevant to the steady state (dynamic equilibrium) and to the evolution of the system towards this steady state. Figure 3 shows that the faster the system tends to the steady state, the higher is the current intensity. In addition the conversion ratio tends to a limit (referred to as X_{eq}) which increases with the current intensity of the discharge (Fig. 5). Similar results are observed for positive discharges (Fig. 4). Reaching the steady state also needs 60-min treatment. The limit X values (referred to as X_{eq}) also depend on the current intensity (Fig. 5). Although some operating parameters may slightly differ, the positive discharge seems to be more efficient than the negative one, since it needs a less important intensity to get the same limiting FC value, X_{eq}.

Figure 4: Evolution with the treatment time t (min) of the FC for various current intensities for a positive corona discharge (d = 15 mm; Q = 500 cm³ s⁻¹; p = 10⁵ Pa.)

Figures 3 and 4 are respectively relevant to negative and positive discharges. They both show that the composition of the gas mixture changes with the treatment time for other given conditions. The conversion ratio X increases with time and tends to a limit: a dynamic equilibrium takes place after about 60-min treatment. This equilibrium is affected by various experimental conditions, as detailed hereafter.

3.5 Influence of the feeding power

The feeding power $P$ may be considered as a more judicious parameter to control the dissociation, because it is connected with the energy provided to the gas in the reactor. Since the
current intensity is an increasing function of the voltage fall (Fig. 2), one can guess that $X_{\text{eq}}$ is again an increasing function of $P/W$. The feature is verified (Fig. 6) on a single plot for discharges of both polarities.

### 3.6 Influence of the electrode gap

The electrode gap $d$ is then considered as a working parameter. We varied $d$ while the current intensity and the gas flow rate were constant. For both discharge polarities, the steady state is reached for at least 40-min treatment. Figure 7 illustrates the variations of the $X$ values with the treatment time for various $d$ values in the case of a positive corona. $X$ tends again to a limit $X_{\text{eq}}$ for 60-min treatments, and this limit increases with the electrode gap (Fig. 8).

For a negative corona discharge, a similar feature is observed (Fig. 8): the plot $X_{\text{eq}}$ vs $d$ is a linearly increasing functions of $d$, with a slope close to $9.3 \times 10^{-4}$ mm$^{-1}$ in the investigated gap range.

Any further comparison is hazardous because the working conditions are too much different and in particular the current intensity. Figure 8 thus suggests that the positive discharge is more efficient than the negative one for the reduction of CO$_2$ to CO. This feature may be first related to electrochemical considerations. In a CO$_2$ atmosphere, only the reduction of CO$_2$ may occur; no oxidation reaction involving the gas has to be considered, since carbon has the highest oxidation state. According to an electrolysis process, the matching oxidation reaction must then concern the metal electrode. An additional argument is related to electrode areas: the area of the plane electrode is much larger than that of the active point, so that the gas molecules in contact with the plane electrode are more numerous than otherwise. For a positive discharge, the plane electrode acts as a cathode, and thus reduction of concerns more numerous CO$_2$ molecules than a negative discharge.

### 3.7 Influence of the plasma energy density $P/N$ [15]

The results above reported involve primary parameters as the working parameters and thus remain immediate. Their interpretation may be improved by considering the plasma energy density $P/N$ that involves the mean energy brought to each gaseous species present in the plasma reactor, the volume of which is defined by the electrode gap and the diameter of the cylinder.

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reasons. Also, when the steady state is reached, $X_{eq}$ depends on the plasma energy density and is close to a linearly increasing function of $P/N$ (Fig. 10) for each discharge polarity. Figure 10 also shows a different behaviour for positive and negative discharges, which may be related to the different flow rates fixed for the experiments, or better to different chemical processes that occur in the reactor.

![Figure 10](image1.png)

**Figure 10:** Variation of the limit FCC (i.e., $100 \times X_{eq}$) with the plasma energy density $P/N$ for negative (a) and positive (b) discharges.

3.8 Influence of the gas flow rate

The influence of the gas flow rate is typically illustrated on figures 11 and 12 for negative and positive discharges respectively. $X_{co}$ increases with the treatment time and tends to the limit value corresponding to the steady state $X_{co\ eq}$ as already mentioned. For various flow rates, the $X_{co\ eq}$ values decrease as the flow rate increases. In other words, the higher is the flow rate, the smaller is the decomposition yield. The $X_{co\ eq}$ values roughly vary with the reverse of the flow rate for both discharge polarities. This feature may be interpreted in terms of interaction between the reagent and the electric field: the longer the reagents remain in the reactor, the higher is the energy transfer and the higher is $X_{co\ eq}$.

![Figure 11](image2.png)

**Figure 11** Variation of the limit mole fraction of CO (i.e., $100 \times X_{co\ eq}$) with the space time for a negative discharge.

![Figure 12](image3.png)

**Figure 12** Variation of the limit mole fraction of CO (i.e., $100 \times X_{co\ eq}$) with the space time for a positive discharge.

3.9 Influence of the space-time

The influence of the gas flow rate may then be considered by means of the space time $t_s$ which is defined as the reactor volume divided by the volume rate of flow [18]. Figure 10 shows that $X$ increases with the space time $t_s$ for a given plasma energy density for both positive and negative discharges.

4. Discussion

4.1 Comparison with other studies

Many authors examined the dissociation of CO$_2$, since it was one of the main reasons for the limitation of the operational life and the loss of performance of CO$_2$ lasers, with the formation of ozone and nitrogen oxides. They were led to consider the mechanism of dissociation, which depends on the working conditions. Several excitation techniques were used, but only a limited number of papers concerns the corona discharge. The authors agree with the occurrence of an equilibrium, as stated by Tanaka et al. [2-4]: the present study confirms this feature in the case of corona discharges operated at atmospheric pressure and for both polarities. Palotai and Chang [13] focused on the influence of the composition of the gas mixture. On adding Argon to CO$_2$ in their capillary reactor with spark discharges device, they found that the CO$_2$ concentration decreases with increasing discharge current and gas flow-rate.
Interested in ozone preparation and considered the influence of CO$_2$ in air on O$_3$ synthesis. The later focused on the influence of the gas flow rate and found that X$_{eq}$ decreases with increasing gas pressure. This result confirms Cenian el al. [23] work on the degradation of laser gas mixtures. Boukhalfa et al. [5] varied the electrode gap and plotted $I$ vs. $U$ in pure CO$_2$ for positive and negative discharges. They found $I_{eq} >> I_{pos}$ for the same electrode gaps, in pure CO$_2$. They also showed that the CO yield in a positive corona is proportional to gap length and they concluded that occurring streamers favour the dissociation of CO$_2$. This survey of the pertinent literature shows that our experimental results satisfactorily agree with the reported data.

4.2 Comparing the CO yields in positive and negative corona treatments

All the experiments reported in this study show that the positive corona discharge is much more efficient than the negative corona to transform Carbon dioxide to monoxide. Assuming that CO$_2$ and CO are the main species concerned in the electrochemical process, in addition to the oxygen species, then classical electrochemistry may bring arguments to explain this unusual feature with reference to the particular symmetry of the device already mentioned.

In a negative discharge, the CO$_2$ molecules are reduced at the point electrode, that is at a surface of small area. At the neighbourhood of this electrode CO$_2$ is reduced to CO and oxygen atoms form. These O atoms either react rapidly to yield oxygen molecules in the electrode gap, or drift to the plane electrode together with the formed CO molecules due to the electric wind. A number of CO molecules may then oxidise at the plane electrode acting as an anode since its surface is much larger. Hence the efficiency of the transform must be poor, and an important part of the feeding energy is spent.

Now, for a positive discharge, the point electrode acts as the anode and has thus a limited interaction with CO$_2$. Most of the CO$_2$ molecules are reduced at the large plane cathode, and the electric wind prevents them from back transferring to the point electrode where they might oxidise.

5. Conclusions

As previously mentioned, the dissociation mechanism of CO$_2$ is mainly considered in studies in connection with gas laser ageing and loss of efficiency. For example, Hokazono et al. [15] list numerous kinetic data, with special emphasis on kinetics involving excited species. Wagner et al. [12] examine the influence of pressure on the decomposition of CO$_2$ in a dielectric barrier discharge reactor. Starting from the existence of Chemical Quasi Equilibria in their reactor, they consider two limit situations according to the concentration $n_e$ of electrons in the plasma: the Chemical Equilibrium of Electronic Catalysis, for $n_e \rightarrow 0$, and the Chemical Equilibrium of Complete Electronic Decomposition, for $n_e \rightarrow \infty$. They report an overall mechanism with 21 elementary reactions and conclude on the occurrence of equilibrium between CO, CO$_2$ and O$_2$ in dielectric barrier discharge conditions.

In the case of d.c. corona discharges, some of the elementary reactions proposed by Wagner et al. [12] probably take place, but complementary electrochemical processes may be also considered. The improved efficiency of barrier discharges may be related to the occurrence of a barrier that separates the compartments and prevents a species transformed at one electrode to undertake the reverse transformation at the other electrode.

The general survey of the working parameters of the corona discharge treatment of CO$_2$ shows that equilibrium takes place, in good agreement with the pertinent literature. This feature may be the key for optimising the processes for various applications in the scope of better and wealthy environment, such as CO$_2$ removal or COX abatement in Volatile Organic Compounds effluents by positive corona or barrier discharges.

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