

Review

Non-Thermal Plasma Technology for CO₂ Conversion—An Overview of the Most Relevant Experimental Results and Kinetic Models

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Abstract: Global warming, along with increasing global energy demands, has led to the need for a sustainable and low-carbon-based energy economy. In addition to renewable energy technologies, such as biomass, solar, hydro, and wind, another possible strategy to mitigate climate change is the capture/conversion and recycling of CO₂. In recent years, many methods for both CO₂ capture (mainly adsorption, absorption, and membrane) and conversion (many electrolysis, catalyst, and plasma) have been investigated. Conversion technology is less studied but seems to be very promising. Within that, non-thermal plasma technology has received much interest because it works at low temperatures and atmospheric pressure, and there is no need for high temperature and high electricity consumption, which are typical of the catalyst and electrolysis conversion processes, respectively. Therefore, in order to optimize this emerging technology, simulative kinetic models have been developed with the aim of maximizing both energy efficiency and CO₂ conversion. In the present paper, an overview of the most common non-thermal plasma technologies was carried out to highlight the advantages and disadvantages of each method. Then, an overview of the most significant kinetic models available in literature was carried out to point out the main reactions occurring during CO₂ conversion and also the parameters that most affect the performance of a plasma reactor during CO₂ conversion. Then, a brief recap of the literature available on economic studies of the plasma process is given.

Keywords: CO₂ capture; hydrogen; biomass gasification; plasma reactor; kinetic models; NTP



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1. Introduction

It is a well-known fact that human activities, such as burning fossil fuels and deforestation, are to blame for global warming and climate change. However, the production and utilization of unlimited electricity is a must for modern civilization, along with the importance of a plan for energy independence and national security for each country. Therefore, it is necessary to look for renewable energy sources and to develop new sustainable processes for supplying energy. In addition to renewable energy technologies, such as biomass, solar, hydro, and wind, another possible strategy to attenuate climate change is the capture/conversion and recycling of CO₂ (such as for the production of value-added chemicals, e.g., formic acid, methanol, and dimethyl ether [1–9]). Removing carbon dioxide (CO₂) is very important, especially because CO₂ is the largest contributor to greenhouse gas emissions (~82%), which contributes significantly to global warming and climate change issues [1,10,11]. In the last years, many methods for both CO₂ capture (mainly adsorption, absorption, and membrane) and conversion (mainly electrolysis, catalyst, and plasma) have been investigated [12–18].

Below, the main technologies to capture CO₂ are quoted: absorption, adsorption, low-temperature, and membrane technology [19–23].

- Absorption technology is considered the most mature process for capturing CO₂. This method is based on chemical solvents; it works at atmospheric pressure and at a temperature in the range of 40–50 °C [24]. Adsorbents with high selectivity for CO₂ are preferable, resulting in higher CO₂ capture. The CO₂ purity achievable is over 95% [25]. The main disadvantages of this technology are the amount of energy required to capture CO₂ (the power consumption is around 0.5 to 0.8 MJ_e/kg CO₂ [26–28]) and the thermal heat required for the regeneration of solvent. Moreover, if sulfur dioxide or dust are contained in the gas mixture, it is mandatory to separate them from the gaseous stream before the absorption column due to the risk of accelerated degradation of the solvents [24].
- Adsorption technology to capture CO₂ was studied for the first time in the mid-1900s when Colburn and Dodge investigated alumina and silica for the removal of CO₂ from the atmosphere of a submarine [29]. Over the last decades, several studies have been carried on to explore the best materials to produce CO₂ capture processes [30–32]. The choice of sorbent strictly affects the performance of the process. Many studies have demonstrated that cheap and readily available natural sorbents (such as CaO) allow good performances, but further studies must be conducted in order to investigate the issues linked to the attrition and deactivation of sorbents [33]. The main obstacles for industrial-scale operations are sorbent decay, attrition, and temperature. In the context of CO₂ capture from biogas, the difficulties with handling, feeding, and tar production that go along with low-quality biomass waste and poisoning due to H₂S must also be taken into account [33,34].
- A low-temperature separation method for capturing CO₂ was deeply investigated by Berstad et al. [35], who proposed a process design for low-temperature separation. First, the gas mixture is dried in order not to have solid formation, and then compressed until 100 bar and cooled to –55 °C. Then, CO₂ is condensed out in a separator. Studies have demonstrated that CO₂ purity in the range of 99.7–99.9 mol% can be reached. The main disadvantage of this technology is the great amount of energy required for the low-temperature processes, which depends on the shaft work of the compression of the feed gas before cooling and the compression train needed for the refrigeration system.
- The membrane process allows the removal of CO₂ from a gaseous stream by means of a selective permeative membrane. Separating CO₂ selectively from mixtures with hydrogen is challenging because CO₂ molecules are much larger than hydrogen ones [36]. Membrane selectivity depends on what material it is made of and also on the pressure difference, which is the driving force that makes the syngas flows across the membrane. The limit of this technology is that it has not been tested on a sufficiently large scale yet, and, moreover, it requires a high cost for the regenerative membrane process while the CO₂ purity reached is almost the same achieved by solvent absorption [37–40].

Adsorption and absorption are the most mature technologies to capture CO₂, after which it can be stored or converted. Studying CO₂ conversion processes seems to be very profitable. In fact, even though not many studies have been carried out on conversion technologies, they clearly demonstrate that this method could reach high results in terms of CO₂ conversion and energy efficiency [41–45].

Catalytic technology to convert CO₂ into methane is already a mature method; however, it is still being investigated in order to overcome some issues, such as lowering the temperature of catalyst activity, testing the stability of the catalyst when poisonous compounds such as H₂S are present, and scaling up the catalytic membrane applications to industrial scale [46]. Recent studies have focused on the integration of catalytic and plasma technologies, with promising results [47,48].

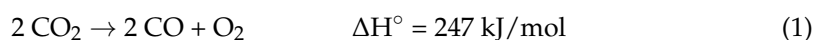
High-temperature electrolysis for CO₂ conversion in solid-oxide electrolysis cells (SOECs) is currently being studied due to its ability to convert CO₂ into valuable fuels through the electrothermal activation of the stable bond between C and O. However, the higher values of conversion and energy efficiency are obtained only when the process is

carried out at high temperature. Moreover, the electrode–electrolyte interface degradation issue needs to be taken into account along with the high electricity consumption required by electrolysis [49].

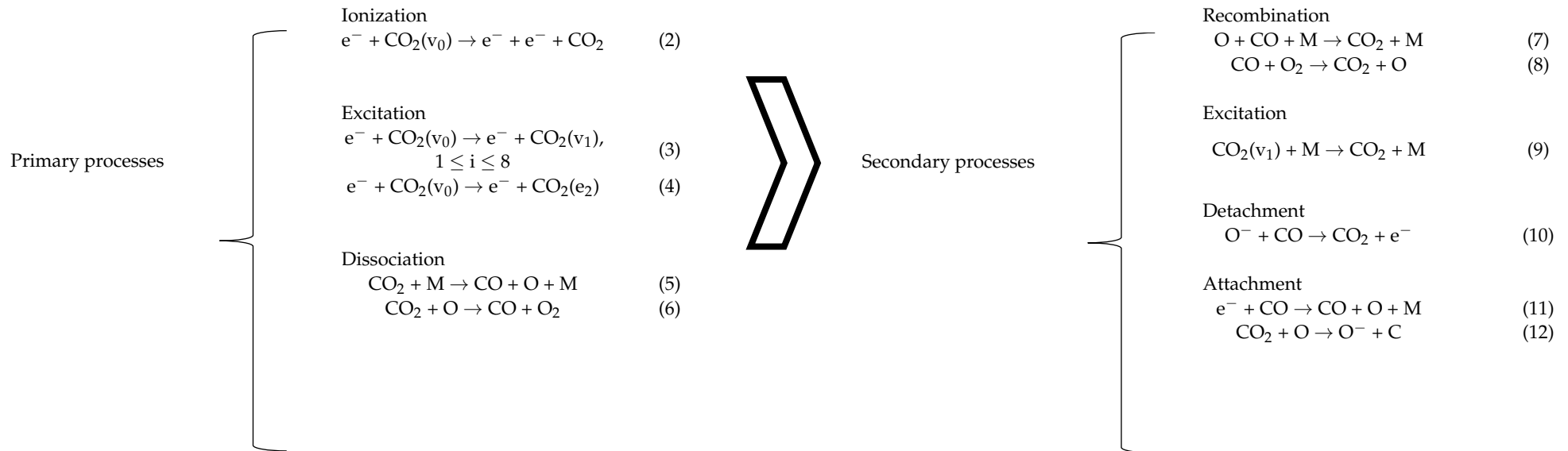
In recent years, a few studies have focused on plasma technology for CO₂ conversion [1,50,51]. Plasma is composed of several reactive species, such as electrons, ions, radicals, and neutral gas molecules, which make it very reactive but not very selective. Plasma chemistry is responsible for the conversion of CO₂ into CO and O₂. Non-thermal plasma (NTP) has received much interest because it has the advantage of operating at room temperature and atmospheric pressure [52]. This technology is very simple compared to other processes, and it has advantages over thermal processes because reaction rates are higher and a steady state is reached faster [53]. Several kinds of NTP technology for CO₂ conversion have been investigated in the recent literature [54–56], and the most promising are dielectric barrier discharge (DBD) [57–61], micro-wave discharge (MWD) [62,63], and gliding arc discharge (GAD) [54]. Plasma is normally created by applying electrical power; however, currently, most electrical power is generated by non-renewable fossil fuels and emits a substantial amount of CO₂ into the atmosphere. In order to avoid this issue, plasma technology fed with renewable energy could be promising if chemical energy storage is localized or distributed into the system during peak grid times, avoiding the issue of high temperature and high energy consumption related to catalyst and electrolysis [52,53]. Therefore, even though it is less studied, the plasma process is predicted to be the most effective [53]. The present review is focused on the most recent studies that applied plasma technology to CO₂ conversion and also the methodology to model such a process.

2. An Overview of NTP Technology for the Conversion of CO₂

The reaction occurring during the decomposition of CO₂ into CO and O₂ is:



In detail, the primary and secondary reactions occurring during plasma-based CO₂ dissociation are [64]:



$\text{M} = \text{CO}_2, \text{CO}, \text{O}_2$

$\text{CO}_2(v_0), \text{CO}_2(v_1)$ and $\text{CO}_2(e_2)$ are the ground state CO_2 , vibrational-excited CO_2 , and electronic-excited CO_2 , respectively.

It is interesting to point out that it is possible to carry out reaction (1) at low temperatures with NTP, which would be impossible using conventional catalytic reactors, which instead work at a very high temperature [65].

The CO dissociated is a valuable product since it is an important chemical feedstock for the further synthesis of fuel and chemicals.

As mentioned above, the most promising NTP technologies for CO₂ conversion are DBD, MWD, and GAD [52]. In the following subsections, a brief description of these methods, along with their advantages and disadvantages, are reported.

2.1. Dielectric Barrier Discharge

A DBD reactor is made of two electrodes set on both sides of a dielectric barrier material, which can be composed of quartz, polymer, glass, etc. A high-voltage AC generator is applied toward the electrodes in order to produce the discharge. A schematic representation of a DBD is shown in Figure 1. The dielectric barrier has the aim of reducing electric current and then inhibiting spark formation [66]. A packed bed DBD is the most common reactor for plasma catalysis [50] since it has a simple design, low operational costs, and offers convenient catalyst integration and easy upscaling [67,68]. On the other hand, DBD reactors are restricted by energy efficiency, which is limited in the actual experiment to below 20% [69]. The parameter that affects the energy efficiency of the process the most is the feed flow rate, while the parameter that has the most influence on CO₂ conversion is the discharge power [70]. Mora et al. [71] demonstrated that using an alumina reactor for DBD plasma rather than quartz has the benefit of increasing CO₂ conversion due to the higher relative dielectric permittivity coefficient of alumina. Moreover, CO₂ conversion can also be favored by the addition of a magnetic field. In order to increase the CO₂ conversion, a regular DBD can be implemented with higher mean electron energies; this method is called Nanosecond Pulsed DBD (NP-DBD) [51]. Bak et al. [72] investigated the conversion of CO₂ using a repetitive NP-DBD (10 nanoseconds), and they achieved a maximum CO₂ conversion and energy efficiency of 7.3% and 11.5%, respectively. Zhou et al. [60] investigated the effect of ZrO₂ pellets in a water-cooled packed-bed DBD reactor and showed CO₂ conversion of up to 50% and energy efficiency of up to 7% compared to 3% without ZrO₂. This result can be attributed both to the lower reaction temperature and higher electron energy. Additionally, Van Laer and Bogaerts [73] showed the efficacy of packing a ZrO₂ bed into a DBD plasma reactor and pointed out that CO₂ conversion and energy efficiency were enhanced up to a factor of 1.9 and 2.2, respectively, compared with the case without zirconia packing. Ashford and Tu [53] evaluated several packing-bed materials in DBD reactors, such as quartz, silica, and CaTiO₃. Their study indicated CaTiO₃ as the best packing material among the ones investigated in the experiments. The CaTiO₃ packing-bed DBD reactor was found to be able to raise CO₂ conversion from 12.5% to 20.5%, and even if the study did not report the energy efficiency, it is possible to calculate it from the data available in Ashford and Tu's paper, obtaining an energy efficiency of 4.8% when the CO₂ conversion is 20.5%.

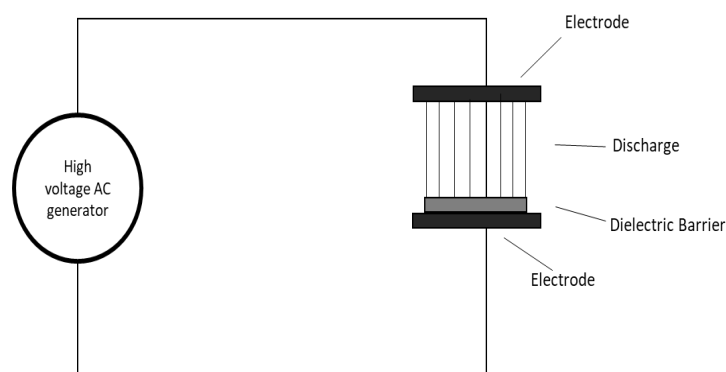


Figure 1. Schematic representation of a DBD.

As mentioned above, the limited energy efficiency is the main restriction of DBD technology, and this is due to the high-energy of electrons generated from the electric field. This is not a suitable condition for the dissociation of CO_2 , which is instead favoured by lower-energy of electrons [52]. Researchers have investigated how to increase reaction performance, and they demonstrated that there is a trade-off between CO_2 conversion and energy [74,75]. Through a few modifications to the plasma system, such as adding a catalyst into the plasma discharge of a DBD reactor, it is possible to increase CO_2 conversion and also to keep a low level of energy consumption, in this way reducing the energy efficiency issue [73,76]. Zeng and Tu [77] investigated the DBD reactor performances, noticing that adding alumina, copper, or manganese catalyst increases CO_2 conversion by up to 4%. However, adding a pure catalyst is expensive (e.g., copper price per 1 kg is USD 7.66, and the other pure catalysts are around that price [78]); therefore, a viable and cheaper alternative to overcome this issue is to mix catalyst with packing material. Mei et al. [79] indicated that packing materials such as barium titanate or quartz wool increase CO_2 conversion and energy efficiency.

2.2. Gliding Arc Discharge

GAD is also called warm plasma technology since it can work at over $800\text{ }^\circ\text{C}$, which means an average temperature among thermal and non-thermal plasma technologies, combining the benefits of the two methods and resulting in higher energy efficiency for CO_2 due to the vibrational excitation of the molecules [80–82]. Many studies have proved that GAD is successful for the vibrational excitation of chemical molecules, and this is considered the most promising way to dissociate CO_2 from the energy point of view [83,84].

A schematic process of GAD is reported in Figure 2. GAD takes place within the reactor, creating a weak ionized gas among the two electrodes, while syngas flows inside the reactor from the electrode base generating a potential difference between the two electrodes. An electric arc discharge is formed across the smallest gap, then it extinguishes, and a new arc is created in the shortest electrode gap. Lastly, the arc voltage slowly grows until the breakdown voltage is reached; from this point on, heat losses become higher than the supplied energy [85,86].

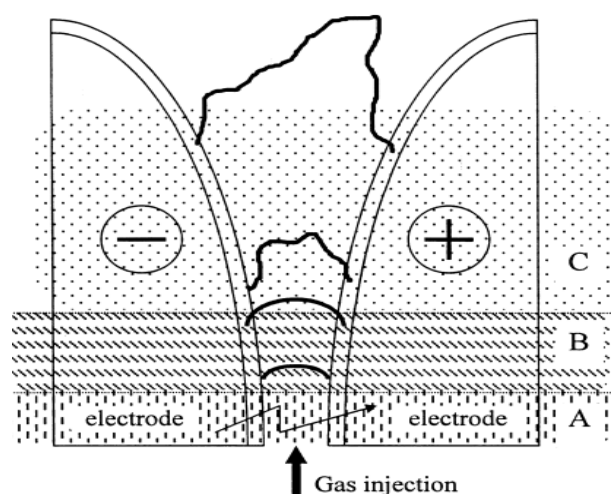


Figure 2. Steps of gliding arc process: (A) reagent gas break-down; (B) equilibrium heating phase; (C) non-equilibrium reaction phase [87].

Indarto et al. [88] investigated how additional gases influence the process of CO_2 conversion using a gliding arc plasma. They demonstrated that if nitrogen is added, the CO_2 conversion reaches 35% when the N_2 concentration is 95%. In contrast, when only pure CO_2 is used, the conversion is at least 18%. They also proved that oxygen and air have a negative effect on CO_2 conversion, and they pointed out that the presence of water reduces

CO₂ conversion. This study obtained promising performances; however, improvements could have been made, such as the addition of catalyst material in order to increase the conversion.

Sun et al. [89] discovered that the main limiting factors for CO₂ conversion when a gliding arc plasma is used are the reverse reactions and the small amount of treated syngas fraction. So, taking into account those restrictions, it is possible to suggest some improvements to the process, such as lowering the temperature of the inlet syngas or raising the power density.

The residence time of the gas is another key parameter in the GAD plasma process. It is inversely proportional to the feed flow rates, and, in fact, when the feed is increased, both the CH₄ conversion and product yields decrease due to the lower chance for the CH₄ molecules to collide with energetic electrons in the plasma zone, which is related to the short residence time. That also means that increasing the feed flow rate reduces the chance of cracking reactions to yield smaller hydrocarbons and carbon. Therefore, in order to obtain the desired products, both the residence time of the feed reactant in the plasma zone and the electric field strength must be well balanced.

Until now, GAD plasma has not been investigated enough, and, in fact, the chemical mechanisms of the reactions are not totally clear. For this reason, in order to increase the conversion of CO₂ while using GAD plasma, it is important to conduct further studies on the physical characteristics of the process by means of electrical measurements, computer simulation, and high-speed photography.

2.3. Microwave Discharge

MWD is a kind of warm plasma that is formed when syngas is exposed to electromagnetic waves in the frequency range of 300 MHz to 10 GHz. Electrodes are not needed in the process. Several types of MWD plasma have been investigated, and surface wave discharge seems to be the most promising for CO₂ conversion [64,90]. Surface wave discharge is obtained when the syngas flows through a quartz tube cut across a waveguide. A schematic representation of MWD is shown in Figure 3.

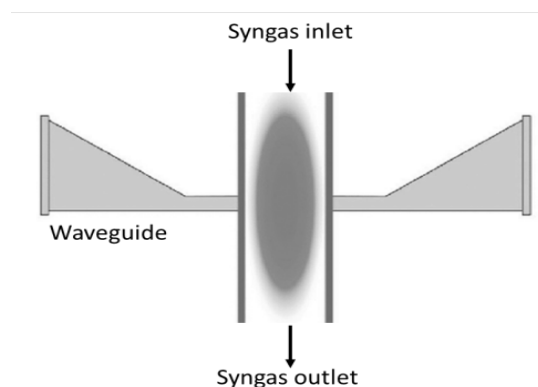


Figure 3. Schematic representation of an MWD.

The plasma goes inside the tube, absorbing the energy produced by the waves to endure itself.

Guoxing et al. [91] evaluated which catalyst has a better influence on CO₂ conversion and energy efficiency using a surface wave MWD. They showed that when using TiO₂ as a plasma catalyst (in Ar gas medium), the CO₂ conversion does not significantly change compared with a plasma-only experiment. Instead, if NiO/TiO₂ is used as a plasma catalyst (in Ar gas medium), both CO₂ conversion and energy efficiency almost double compared with a plasma-only experiment. Using NiO/TiO₂ (in O₂ gas medium) and NiO/TiO₂ (in CO₂ gas medium) as a plasma catalyst does not improve CO₂ conversion and energy efficiencies.

Belov et al. [92] investigated the best configuration for the MWD plasma reactor to maximize CO₂ conversion and energy efficiency. They investigated three conditions, direct gas flow, reverse gas flow, and vortex gas flow, using pure CO₂ and varying pressure from 200 mbar to 1 bar. In the case of direct gas flow, without discharge cooling, the gas temperature is up to 800 °C. That is a favourable temperature for the recombination of CO into CO₂, and, as a consequence, both CO₂ conversion and energy efficiency are very low, 3.5% and 2%, respectively, at 200 mbar. A better configuration was found to be the reverse gas flow coupled with discharge cooling, which allowed CO₂ conversion and energy efficiency up to 38% and 23% at 200 mbar and up to 6.2% and 3.7% at 1 bar. However, the highest values of CO₂ conversion and energy efficiency at atmospheric pressure are given by the vortex flow gas configuration. The authors also highlighted that pressure is inversely proportional to CO₂ conversion and energy efficiency, even if this effect is less significant with vortex flow gas configuration. Another interesting aspect pointed out is that post-discharge cooling has a fundamental role in CO₂ conversion and energy efficiency since lower temperatures avoid the recombination of CO into CO₂.

Among MWD's benefits is the lower chance of contamination or damage compared to DBD and GAD, since it does not include electrodes for discharge, and also the lower cost, since the magnetron used is available on the market; therefore, it is possible to obtain low electric energy cost and high productivity [93].

The parameters that influence the process of CO₂ conversion using MWP the most are power supply, pressure, gas flow rate, and catalyst [63,92,94].

2.4. Comparative Analysis

Summarizing the advantages and disadvantages of DBD, GAD, and MWD plasma reactors, we can say that:

- DBD plasma reactors work at close to ambient temperature and pressure, have low operational costs, and offer a simple design that can easily be upscaled and integrated with a catalyst. For this reason, DBD plasma is the most common plasma technology. However, this technology has the main disadvantage of restricted energy efficiency (2–20%), which could be overcome by adding catalysts and lowering electron excitation.
- GAD plasma reactors work at ambient pressure, offering good energy efficiency (40–60%). The main restriction of this technology is the short residence time of the to-be-treated gas and the low conversion, especially with pure CO₂. Moreover, GAD plasma has not been investigated enough, and, in fact, the chemical mechanisms of CO₂ conversion are not totally clear. For this reason, in the future, more studies should be carried out on the development of chemical kinetics models to understand the reaction mechanisms in plasma CO₂ dissociation.
- MWD plasma reactors work at atmospheric pressure and temperature above 2000 °C. Under these conditions, they offer energy efficiency of up to 40%. The energy efficiency can go up to 90% under certain operating conditions (such as supersonic gas flow and reduced pressure). In order to achieve those conditions, a pressure difference is applied over a converging–diverging nozzle. The adiabatic expansion of the nozzle cross-section accelerates the flow to supersonic velocities. In this way, the acceleration to supersonic speed creates a pressure drop from high-pressure conditions (≥ 1 bar) to an intermediate pressure (around 100 mbar); the latter is advantageous for energy-efficient conversion. Moreover, the fast increase in kinetic energy decreases the internal energy of the gas, thus lowering the temperature and allowing the use of higher power densities, which is also advantageous for energy-efficient CO₂ conversion. Due to high temperature, this technology does not allow easy implementation of catalysts. A solution could be to add catalytic material downstream of the MWD plasma. Until now, there has been no commercialized MWD plasma, but only at a lab scale due to both technical and economic issues. The process still needs to be optimized in terms of MW power, co-reactants, and gas flow rate. Moreover, the MWD plasma reactor is cumbersome, so it is not so easy to upscale. The development of further simulative

models can be useful to better understand the reaction mechanism of MWD plasma in order to optimize the process.

3. Simulative Models

To better understand the behaviour of plasma during CO₂ dissociation and to optimize the process from the point of view of energy efficiency and CO₂ conversion, it could be very useful to propose a simulative approach. Until now, only a few researchers have developed simulative models for plasma reactors to investigate CO₂ conversion [83,95–108].

3.1. Kinetic vs. Thermodynamic Modeling on CO₂ Dissociation

Pietanza et al. [90] offered an interesting comparison between kinetic and thermodynamic modelling approaches in the MWD plasma process at high temperature for CO₂ conversion. The kinetic model developed by the authors considered not only the kinetic of CO₂ but also CO and O₂. The developed model is zero dimension (0D), it neglects any spatial variations, and is time-dependent. The reactions considered by the authors are electron impact reactions, heavy-particle chemical, and vibrational reactions. Additionally, electronically excited states, optical transitions, and quenching processes were taken into account. The kinetic constant of each reaction was taken from previous experimental studies [109–111]. The model was applied to the description of the experimental conditions tested by Groen et al. [112], who performed not only an experimental approach but also a modelling approach, developing a 3-dimensional electromagnetic simulation that is able to evaluate the reduced electric field. Comparing the results from Groen et al. [112] and Pietanza et al. [90], it is possible to notice that electron density, reduced electric field, and electron temperature are in good agreement, even if the 0D model assumes a constant power density while the 3D model does not. Comparing kinetic and thermodynamic equilibrium results, it is possible to point out that the majority species are in good agreement, but the minority ones are not. Results showed a large difference in carbon molar fraction between the kinetic and thermodynamic methods. This behaviour may be due to the neglect of the Boudouard reaction, responsible for forming carbon and carbon dioxide, in the case of the thermodynamic approach. The comparison of Groen et al. [112] and Pietanza et al. [90] suggests that the thermodynamic equilibrium approach must be implemented cautiously because the calculated results, which are quite different from the results obtained by the kinetic approach, affect the plasma parameters and, therefore, the future applications. On the other hand, it is not easy to find all the kinetic constants and rate coefficients since the plasma process has not been deeply investigated yet.

3.2. Literature Kinetic Models

The first simulative model was developed by Rusanov and Fridman [113,114]. They implemented an analytical model to describe and solve the vibrational distribution functions and energy conservation equations in the case of an MWD plasma reactor. The results for CO₂ conversion and energy efficiency were in good agreement with experimental testing; however, the model was very simplified and neglected the plasma chemistry, and did not offer a proper determination of the electron density.

Aerts et al. [101] developed a 0D, time-dependent, kinetic model in order to investigate the reaction mechanisms that take place during CO₂ conversion in a DBD plasma reactor. The real volume of all micro-discharges is smaller compared to the plasma reactor; therefore, in the model, the assumption to multiply the power density by a factor of 7 was made. Actually, the true plasma volume was not known, and 7 is a value that was chosen arbitrarily to reproduce experimental data. This assumption did not affect the results, as shown by the comparison with experimental data. The model analysed is a simplification of a previous model developed by the author [115] in which 42 species were taken into account, and 501 chemical reactions took place. In the new simplified version, only 9 species and 17 chemical reactions are considered, which are the most critical plasma species and reactions for CO₂ dissociation. The reactions included are shown in Table 1. This study

pointed out that electron-impact dissociation, electron-impact ionization, and dissociative attachment are mainly responsible for CO₂ conversion.

Table 1. Chemical reactions considered in the simplified kinetic model of [101] and corresponding rate coefficients (which are described as cm³s^{−1} for the two-body reactions and as cm⁶s^{−1} for the three-body reactions).

Entry	Reaction	Rate Coefficient
1	$e^- + \text{CO}_2 \rightarrow \text{CO}_2^+ + 2e^-$	5.4×10^{-11}
2	$e^- + \text{CO}_2 \rightarrow \text{CO} + \text{O} + e^-$	5.8×10^{-11}
3	$e^- + \text{CO}_2 \rightarrow \text{CO} + \text{O}^-$	7.0×10^{-12}
4	$e^- + \text{O}_3 \rightarrow \text{O} + \text{O}_2 + e^-$	2.0×10^{-9}
5	$e^- + \text{O}_2 \rightarrow \text{O} + \text{O} + e^-$	2.0×10^{-9}
6	$e^- + \text{O}_2 \rightarrow \text{O} + \text{O}^-$	4.0×10^{-11}
7	$e^- + \text{O}_2 + \text{M} \rightarrow \text{O}_2^- + \text{M}$	3.0×10^{-30}
8	$\text{O}^- + \text{CO} \rightarrow \text{CO}_2 + e^-$	5.5×10^{-10}
9	$\text{O}^- + \text{O}_2 \rightarrow \text{O}_3 + e^-$	1.0×10^{-12}
10	$\text{O}^- + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + e^-$	3.0×10^{-10}
11	$e^- + \text{CO}_2^+ \rightarrow \text{CO} + \text{O}$	6.5×10^{-7}
12	$\text{O}_2^- + \text{CO}_2^+ \rightarrow \text{CO} + \text{O}_2 + \text{O}$	6.0×10^{-7}
13	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$5.2 \times 10^{-35} \exp(900/\text{T}[\text{K}])$
14	$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	$4.5 \times 10^{-34} \exp(\text{T}[\text{K}]/298)^{-2.70}$
15	$\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$	$8.0 \times 10^{-12} \exp(-17.13/\text{T}[\text{K}])$
16	$\text{O} + \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$1.7 \times 10^{-33} \exp(-1510/\text{T}[\text{K}])$
17	$\text{O}_3 + \text{M} \rightarrow \text{O}_2 + \text{O} + \text{M}$	$4.1 \times 10^{-10} \exp(-11,430/\text{T}[\text{K}])$

Kozák and Bogaerts [100] started from the kinetic model of Aerts et al. [101], adding a set of CO₂ vibrational levels. The model, which is a 0D, is able to perform the dissociation of CO₂ in non-equilibrium plasma under high excitation of vibrational level. The numerical solution of the developed model was given by the global kin code created by [116]. The authors simulated the process of CO₂ conversion in two configurations in an MWD plasma reactor and in a DBD plasma reactor. The results of their investigation confirmed that the MWD reactor could reach higher values in terms of CO₂ conversion and energy efficiency than the DBD reactor. Moreover, the authors found that CO₂ conversion and energy efficiency in DBD reactors are higher when there are no CO₂ vibrational levels. This behaviour is related to the fact that no energy is wasted at the entrance of the reactor, unlike when there are vibrational excitations, which are not favourable for CO₂ conversion. However, the aim of the authors was not to obtain a faithful reproduction of reality based on an experimental setup. The aim was to create a simple, trustworthy model to demonstrate the main mechanism that occurs during the CO₂ dissociation process in the two configurations of discharges analysed. For this reason, the model presents many simplifications and neglects, such as the assumption of keeping constant the plasma parameters orthogonal to the tube axis. Even if the results could not fully reproduce the experimental results, the general trends were still in good agreement, indicating that the main physic and chemical aspects were well included in the model. Nevertheless, this simplified model, which was applied only for two specific configurations, cannot be considered a general conclusion for all the possible configurations. However, this study gave the first raw investigation on the influence of discharge conditions on vibrational kinetic and on principal separation mechanisms.

Heijkers et al. [117] developed a 0D kinetic model to evaluate CO₂ conversion and energy efficiency for a CO₂/N₂ MWD plasma reactor taking into account the vibrational levels of both carbon dioxide and nitrogen. Balance equations were used to determine the evolution during the time of the species' densities. Many assumptions were established in the model, such as the neglect of transport phenomena and the assumption of keeping the plasma volume and the rate coefficients of the reactions constant. The comparison of simulative results with experimental values offered an agreement within only 23% for CO₂ conversion. However, this study is helpful in understanding the key role of nitrogen in populating the carbon dioxide vibrational levels, explaining the higher CO₂ dissociation when N₂ is added. However, the study demonstrated that increasing the N₂ fraction over a certain value (around 10%_{v,ol}) causes a decrease in both CO₂ conversion and energy efficiency because there is less CO₂ in the inlet gaseous mixture stream.

Snoeckx et al. [69] developed a plasma chemistry set based on experimental results taken from literature studies. The 0D kinetic model developed was used to investigate the influence of H₂O on CO₂ conversion in a DBD plasma reactor, and it was found that the conversion of CO₂ decreases with an increase in water. This trend is due to the OH radicals, which recombine with CO into CO₂, causing the limitation of CO₂ conversion when water is added.

Alliati et al. [66] improved the already existing 0D DBD plasma reactor kinetic models taking into account the effect of the experimental parameters (e.g., discharge power, flow rate, etc.). The plasma chemistry set was based on the study of [115], and the CO₂ electron impact dissociation rate coefficients were taken from the study of [118]. The developed model provided interesting results that are useful for better understanding why the energy efficiency is so low when it comes to a DBD plasma reactor. Analyzing the data from this study, it is possible to conclude that most of the energy at the entrance is wasted due to vibrational excitations that do not favour the separation of CO₂.

Wang et al. [119] developed a 2D model which took into account vibrational kinetics to describe CO₂ conversion in a GAD plasma reactor using as a chemistry set the 0D model of Kozák and Bogaerts [100] but reducing it to its main species and chemical reactions in order to avoid long computational times. This model was able to give an insight into the phenomenon and also pointed out the restricting parameters for CO₂ dissociation. The study demonstrated that CO₂ conversion is favoured by its vibrational levels, which is in good agreement with the experimental values that indicate GAD plasma is the most efficient in terms of energy efficiency compared with other plasma technologies. The importance of CO₂ vibrational levels has to be taken into account for further improvements of the GAD plasma reactor in order to optimize this technology with the aim of maximizing energy efficiency.

4. Overview of the Economic Impact and Power Consumption

Until now, very few studies have been conducted about power consumption and the economic impact of NTP technologies, and only a small number of those studies are economic assessments that investigate the profitability of large-scale applications. Those few studies point out that scaling up plasma technology requires high energy input for continuous plasma generation. Nevertheless, the required electrical power can be provided through renewable sources of energy (e.g., solar, wind, and hydro) in order to improve performance environmentally and economically.

Although there is a lack of economic analysis studies in the literature, Rooji et al. [120] carried out a realistic process design of microwave plasma for CO₂ conversion into pure CO, and they used that study for an economical investigation. The aim was to scale up the MWD to a typical commercial size for a plant that produces 20,000 tons/year of pure CO. In order to achieve the required power, they combined 264 commercially available MWD reactors of up to 0.5 MW. The authors delivered a cost analysis for all the equipment and reported the following values: USD 7.2 M for microwave generators and USD 23 M for plasma generators, obtaining a total plant Capital Expenditure (CAPEX) of USD 30.2 M. Then, they

made an assumption considering that, due to the improvement in semiconductor-based microwave generators, it is likely that the cost of industrial plasma generators will be around USD 0.05/W in the near future. With this assumption, the overall CAPEX would be around USD 9 M, which is almost half of the cost needed for a 20,000 ton/year CO plant based on conventional technology and feedstock. The electricity price assumed for the study was ~50 USD/MWh, which is almost half of the total operative cost.

Pou et al. [121] investigated the efficiency of a fluidized plasma reactor for CO₂ conversion into CO, taking into account two scenarios: using electricity from the grid (derived from a mix of renewables and fossil fuels) and full photovoltaic electricity. The aim of the study was to demonstrate the economic benefit of feeding plasma with renewable energy sources. The CO₂ flow rate was fixed at 10 mL/min, and CO₂ conversion was 41%. In the first scenario, in which a mix of electricity was used to feed the plasma reactor, the compensation of CO₂ emissions was 3%, which means only 3% of the CO₂ emissions can be compensated by the process, and the consumption of energy was 0.11 kWh per gram of CO₂ converted into CO. The emissions associated with electricity consumption were 32 g CO₂-eq/kWh. In the second scenario, in which photovoltaic electricity was used to feed the plasma reactor, the compensation of CO₂ emissions was 67%. This is significantly increased compared to the first scenario, which means that coupling NTP technology with renewable energy sources increases the sustainability of the process. The emission associated with the consumption of electricity was 22 g CO₂-eq/h.

Butterworth et al. [74] published a valuable study regarding power consumption. They monitored the power consumption of a lab-scale DBD plasma reactor, varying the packing-bed materials. When the feed gas flow rate was set at 100 mL/min of pure CO₂, they demonstrated that the packing bed does not affect the plasma power but only the CO₂ conversion. For instance, using spherical materials of BaTiO₃ in one test and Al₂O₃ in another one and changing the diameter range from 180 to 2000 µm, plasma power was not severally influenced by the dimension of the packed-bed material or by the different materials, while the CO₂ conversion strictly depends on those parameters.

- Using spherical BaTiO₃ (diameter range: 1400–2000 µm), the maximum value of CO₂ conversion obtained is 2%, corresponding to a plasma power of around 13 MW.
- Using spherical Al₂O₃ (diameter range: 1400–2000 µm), the maximum value of CO₂ conversion obtained is 1.4%, corresponding to a plasma power of around 13.
- Using spherical BaTiO₃ (diameter range: 850–1400 µm), the maximum value of CO₂ conversion obtained is 1.2%, corresponding to a plasma power of around still 13 MW.
- Using spherical Al₂O₃ (diameter range: 850–1400 µm), the maximum value of CO₂ conversion obtained is 0.5%, corresponding to a plasma power of around still 13 MW.

Biset-Peirò et al. [122] investigated the link between plasma power and temperature in a DBD plasma reactor considering two configurations (pseudo-adiabatic and adiabatic) and imposing a gas flow rate of 150 mL/min⁻¹ composed of an H₂/CO₂ mixture (H₂:CO₂ = 4:1). In both tests, the temperature increased with the increase in plasma power, going from 150 to 350 °C in the adiabatic test and from 50 to 150 °C in the pseudo-adiabatic test, when plasma power went from 5 to 15 W. No external heat was added. The maximum CO₂ conversion found in the pseudo-adiabatic configuration was 75%, and it was obtained when plasma power was at 20 W. The same conversion was obtained at lower plasma power in the adiabatic configuration (8.5 W), and the highest CO₂ conversion found in the adiabatic configuration was obtained at 12.5 W. In both the adiabatic and pseudo-adiabatic configurations, the temperature reached was enough to activate the conversion reaction by the thermal catalyst. The tests highlighted that using a DBD plasma reactor in an adiabatic configuration rather than the pseudo-adiabatic configuration increases the energy efficiency by 20% and reduces the cost due to the lower plasma power required. Indeed, working at adiabatic conditions is energetically less demanding because of the synergetic effects between plasma and thermal activation.

5. Conclusions

Non-thermal plasma technology has been demonstrated to be advantageous over thermal processes due to higher reaction rates and faster reaching of steady state. Moreover, compared to other conversion processes, it does not require the continuous electric current consumption of electrolysis or the high temperature of the catalyst process. For these reasons, non-thermal plasma technology seems to be a very promising solution for CO₂ conversion, even if it still has less conversion and energy efficiency than catalyst and electrolysis. This is why a deep comprehension of the plasma chemistry and kinetic models is needed to highlight and develop the most relevant processes that lead to CO₂ conversion. Kinetic models are preferred over fluid models because the computational costs are lower, and the results still present a good agreement with experimental data. 2D or 3D kinetic models may provide better insight into the process; however, they are generally not practical since they need to describe the locations and velocities of all the plasma particles, and also all the chemical reactions involved must be reported. Therefore, it is most common to use the 0D kinetic model, which neglects any spatial variations. The modelling approach not only helps to investigate the chemical plasma mechanism during CO₂ dissociation but also to optimize the process from the point of view of energy efficiency and CO₂ conversion. For example, models have shown that adding N₂ increases the carbon dioxide vibrational levels, and for this reason, CO₂ dissociation is favored; therefore, it can be used as an additive during the design of the real plant. In the same way, since kinetic models showed that the conversion of CO₂ decreases with an increase in water due to the OH radicals, which recombine with CO into CO₂, causing the limitation of CO₂ conversion, the water should be eliminated. Thus, models demonstrate how to avoid losses of energy efficiency and CO₂ conversion; however, the importance of CO₂ vibrational levels has to be taken into account in order to reach high conversion and efficiency levels. Further studies must be carried out on the DBD plasma reactor in order to overcome the issue of its low energy efficiency, which is due to the waste of energy input related to vibrational excitation. There are still many plasma mechanisms that are not clear yet. However, since literature studies have pointed out that electron-impact dissociation, electron-impact ionization, and dissociative attachment are mainly responsible for CO₂ conversion, further studies should be conducted on these aspects to investigate them better to optimize the CO₂ dissociation process.

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