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Modeling for a Better Understanding of Plasma-Based CO₂ Conversion

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Abstract

This chapter discusses modeling efforts for plasma-based CO₂ conversion, which are needed to obtain better insight in the underlying mechanisms, in order to improve this application. We will discuss two types of (complementary) modeling efforts that are most relevant, that is, (i) modeling of the detailed plasma chemistry by zero-dimensional (0D) chemical kinetic models and (ii) modeling of reactor design, by 2D or 3D fluid dynamics models. By showing some characteristic calculation results of both models, for CO₂ splitting and in combination with a H-source, and for packed bed DBD and gliding arc plasma, we can illustrate the type of information they can provide.

Keywords: CO₂, plasma chemistry, plasma reactor, fluid dynamics modeling, chemical kinetic modeling

1. Introduction

In recent years, there is increasing interest in plasma-based CO₂ conversion [1]. Several types of plasma reactors are being investigated for this purpose, including (packed bed) dielectric barrier discharges (DBDs) [2–10], microwave (MW) plasmas [11–13], and ns-pulsed [14], spark [15], and gliding arc (GA) [16–20] discharges. Research focuses on pure CO₂ splitting into CO and O₂, as well as on mixtures of CO₂ with a hydrogen source, such as CH₄ but also H₂O or H₂, to produce value-added chemicals like syngas, hydrocarbons, and oxygenated products. Key performance indicators are the conversion and the energy efficiency of the process, as well as selectivity to produce specific value-added chemicals. To realize the latter, the plasma should be combined with a catalyst (e.g., [3–5, 21]), as the plasma itself is a too reactive environment and thus not selective.

To improve the application, a good insight in the underlying mechanisms is crucial. This can be obtained by experiments, but modeling the plasma chemistry and reactor design can be a valuable alternative, as it provides information on the most important chemical reaction pathways and on how the geometry and operating conditions can be optimized to improve the results.

In this chapter, we will describe the basics of both plasma chemistry modeling (typically based on 0D chemical kinetic models) and plasma reactor modeling

(typically based on 2D, or even 3D, fluid models), and we will show some characteristic examples from our own research, to illustrate how such models can give more insight in the underlying mechanisms. First, however, we will present a brief overview of the different models relevant to CO₂ conversion that have been reported in literature.

2. Literature overview on modeling for plasma-based CO₂ conversion

Describing a detailed plasma chemistry in 2D or 3D models, with 100s of species and chemical reactions, is not yet feasible, due to excessive calculation times. Therefore, a detailed plasma chemistry is typically described by 0D chemical kinetic models or sometimes by 1D fluid models. The first papers on CO₂ plasma chemistry modeling were published back in 1987–1995 but were applied to CO₂ lasers [22–24]. Some papers also studied the vibrational kinetics of CO₂ for gas flow applications [25, 26]. Rusanov et al. [27] were the first to develop a model for CO₂ conversion in a MW plasma, based on particle and energy conservation equations for the neutral species, and an analytical description of the vibrational distribution function.

In the last decade, the research on plasma-based CO₂ conversion experienced a clear revival, and quite some plasma chemistry models have been developed in literature, for either pure CO₂ splitting [7, 28–48] or CH₄ (of interest for hydrocarbon reforming) [49–52], as well as in various mixtures, that is, CO₂/CH₄ [53–66], CH₄/O₂ [66–72], CO₂/H₂O [73], and CO₂/H₂ [74, 75], of interest for producing value-added chemicals, or in mixtures of CO₂/N₂ [76, 77] or CH₄/N₂ [78–83], more closely mimicking reality, as N₂ is a major component in effluent gases. Recently, we gave an overview of such 0D models for plasma-based CO₂ and CH₄ conversion [84], and we also presented a very comprehensive plasma chemistry model for CO₂ and CH₄ conversion in mixtures with N₂, O₂, and H₂O [85]. These plasma chemistry models can provide detailed information on the underlying chemical reaction pathways for the conversion or product formation.

Furthermore, to investigate which reactor designs can lead to improved CO₂ conversion, 2D or even 3D fluid models can be used; they offer a good compromise between level of detail and calculation time. To our knowledge, the number of 2D models for describing CO₂ conversion is very limited [86, 87], and there exist no 3D models yet for this purpose. Most of the 2D/3D fluid models developed up to now in the literature for the typical plasma reactors used for CO₂ conversion are developed in argon or helium, or sometimes air, with limited chemistry, to reduce the calculation time.

For packed bed DBD reactors, different types of modeling approaches have been developed. Chang [88] presented a 0D plasma chemistry model, simply predicting the enhancement factor of the electric field in the voids between the packing pellets from the ratio of the dielectric constant of the pellets and the gas phase. Takaki et al. [89] applied a simplified time-averaged 1D model in N₂, based on solving the transport equations and Poisson's equation. Zhang et al. [90] performed 2D particle-in-cell/Monte Carlo collision (PIC/MCC) simulations for the filamentary discharge behavior in a parallel-plate packed bed DBD reactor in air. Kang et al. [91] developed a 2D fluid model for a DBD with two stacked ferroelectric beads and studied the propagation of the microdischarges, but no plasma species were explicitly considered. Russ et al. [92] applied a 2D fluid model for studying transient microdischarges in a packed bed DBD operating in dry exhaust gas. Based on a 2D fluid model for a packed bed reactor with dielectric rods, Kruszelnicki et al. [93] presented a very interesting and detailed study on the mechanism of discharge

propagation in humid air, reporting that the discharges can generally be classified in three modalities: positive restrikes, filamentary microdischarges, and surface ionization waves. They observed that the type of discharge dominating the production of reactive species depends on the dielectric facilitated electric field enhancement, which is determined by the topography and orientation of the dielectric lattice. Finally, they demonstrated that photoionization plays an important role in discharge propagation through the dielectric lattice, because it seeds initial charge in regions of high electric field, which are difficult to access for electrons from the main streamer [93]. Van Laer et al. [94–96] developed two complementary 2D fluid models to describe a packed bed DBD in helium, to elucidate the electric field enhancement between the packing beads, and the effect of the dielectric constant of the packing beads, as well as the gap size and bead size. Wang et al. [97] applied a 2D fluid model to a packed bed DBD in air, studying the behavior of positive restrikes, filamentary microdischarges, and surface discharges, as well as the transition in discharge modes upon changing the dielectric constant of the packing beads. Finally, Kang et al. [98] also presented a 2D fluid model to study surface streamer propagation in a simplified packed bed reactor, in comparison with experimental data, obtained from time-resolved ICCD imaging.

For MW plasmas, a large number of models were presented in the literature, and we refer to [99] for a recent overview. Van der Mullen et al. [100–102] as well as Graves et al. [103] developed self-consistent 2D fluid models, based on Maxwell's equations for the electromagnetic field and plasma fluid equations, assuming ambipolar diffusion. Some of these models were applied to intermediate pressure coaxial microwave discharges [102], while others describe atmospheric pressure cylindrical (surfaguide or surfatron) MW plasmas [101, 103]. Although being very valuable, these models did not apply to the application of CO₂ conversion. Recently, Georgieva et al. [99] performed a comparison between two fluid models, based on the coupled solution of the species conservation equations and Poisson's equation (i.e., so-called non-quasi-neutral approach) on the one hand and on a quasi-neutral approach on the other hand, but again these models were developed for argon.

For low-current nonthermal GA discharges (typically near 1 A or below), some simple 1D analytical or semi-analytical models have been developed [104–109], including the plasma string model [104] and the Elenbaas-Heller model, assuming an equilibrium plasma, with the radius of the plasma channel being constant [105–107] or with a correction based on an analytical relation between the electric field and the electron and gas temperatures for non-equilibrium plasma [108] or focusing on the discharge electrical parameters [109]. These simple models cannot describe the complex behavior of the GA, such as the unsteady behavior in time and space, arc restrike, non-equilibrium effects, effects of flow patterns, etc., and they did not include a detailed chemistry. Gutsol and Gangoli [110] presented a simple 2D model of a GA, in a plane parallel to the gas flow and perpendicular to the discharge current, which provided very useful information about the gas-discharge interaction. Within our group, we developed a 2D non-quasi-neutral fluid model for the arc gliding process in an argon GA [111], and we compared the glow and arc mode in this setup [112]. We also presented a 2D quasi-neutral model [113], which was also applied in 3D modeling for a classical (diverging electrode) GA [114] and a reverse vortex flow (RVF) GA (also called GA plasmatron; GAP) [115]. These models were developed for argon, but we also developed a 1D fluid model [44] and two different 2D models [86, 87] for a (classical or RVF) GA in CO₂, considering the detailed plasma chemistry of CO₂ conversion. An overview of both 0D chemical kinetic models and 2D/3D fluid models for plasma reactors of interest for CO₂ conversion was presented in [116].

3. Explanation of the modeling approaches

3.1 0D chemical kinetic modeling

Most models describing a detailed plasma chemistry apply the 0D chemical kinetic approach, which allows to handle a large number of species and chemical reactions, with limited computational effort. This approach is based on solving balance equations for the various species densities, based on production and loss rates, as defined by chemical reactions:

$$\frac{dn_i}{dt} = \sum_j \left\{ \left(a_{ij}^{(2)} - a_{ij}^{(1)} \right) k_j \prod_l n_l^{a_{lj}^{(1)}} \right\} \quad (1)$$

where $a_{ij}^{(1)}$ and $a_{ij}^{(2)}$ are the stoichiometric coefficients of species i , at the left- and right-hand sides of a reaction j , respectively, n_l is the species density at the left-hand side of the reaction, and k_j is the rate coefficient of reaction j . For the electron reactions, the energy-dependent rate coefficients are determined from the average electron energy, while the rate coefficients of the chemical reactions between neutral species or ions are adopted from the literature.

The species typically included in such models, for either pure CO_2 or pure CH_4 , as well as the extra species included in CO_2/CH_4 , $\text{CO}_2/\text{H}_2\text{O}$, CO_2/H_2 , or CH_4/O_2 gas mixtures and in CO_2/N_2 and CH_4/N_2 mixtures are listed in **Table 1**. The same species can be included in the CO_2/CH_4 , $\text{CO}_2/\text{H}_2\text{O}$, CO_2/H_2 , and CH_4/O_2 models, because these combinations produce similar molecules. All the species listed in **Table 1** might chemically react with each other. Hence, a large number of chemical reactions (typically up to 1000) are incorporated in these models, including electron impact reactions, electron-ion recombination, and ion-ion, ion-neutral, and neutral-neutral reactions. Details of these chemistries for the specific gas mixtures can be found, for example, in [7, 28–30, 61–63, 66, 73–77, 83].

Specifically for CO_2 conversion in MW and GA plasmas, the vibrational levels of CO_2 are very important, because they allow energy-efficient CO_2 conversion [117], so the vibrational kinetics of CO_2 must be incorporated and especially the asymmetric stretch mode of CO_2 , which is the most important channel for dissociation [117]. Likewise, in CO_2/N_2 mixtures in MW or GA discharges, the N_2 vibrational levels must be included, as they can populate the CO_2 vibrational levels [76]. Furthermore, also the vibrational levels of CO and O_2 , and some electronically excited levels, are typically taken into account in such models (see **Table 1**). These vibrationally and electronically excited levels are indicated in **Table 1** with the symbols “V” and “E”. Details about their notations can be found in [29, 76] or in **Table 1** for the N_2 electronically excited levels. Although vibrationally excited levels might also be important for CH_4 , H_2O , and H_2 molecules, they are not yet included in the available models, to our knowledge, as these mixtures have only been described up to now for a DBD plasma, where the vibrational levels are of minor importance [117].

Although the above balance equations only account for time variations, thus neglecting spatial variations due to transport in the plasma, spatial variations can be included in such models, by imposing a certain input power or gas temperature as a function of time. For instance, this allows to account for microdischarge filaments in a DBD, through which the gas molecules pass when flowing through the reactor, by applying a number of pulses as a function of time (see, e.g., [28, 48, 62]). In a similar way, this method can account for the power deposition profile in a MW plasma (being at maximum at the position of the waveguide) by means of a temporal profile. Thus, the plasma reactors are considered as plug flow reactors, where

Molecules	Charged species	Radicals	Excited species
Species of interest in pure CO ₂ models			
CO ₂ , CO	CO ₂ ⁺ , CO ₄ ⁺ , CO ⁺ , C ₂ O ₂ ⁺ , C ₂ O ₃ ⁺ , C ₂ O ₄ ⁺ , C ₂ ⁺ , C ⁺ , CO ₃ ⁻ , CO ₄ ⁻	C ₂ O, C, C ₂	CO ₂ (Va, Vb, Vc, Vd), CO ₂ (V1-V21), CO ₂ (E1, E2), CO(V1-V10), CO(E1-E4)
O ₂ , O ₃	O ⁺ , O ₂ ⁺ , O ₄ ⁺ , O ⁻ , O ₂ ⁻ , O ₃ ⁻ , O ₄ ⁻	O	O ₂ (V1-V4), O ₂ (E1-E2)
	Electrons		
Species of interest in pure CH ₄ models			
CH ₄	CH ₅ ⁺ , CH ₄ ⁺ , CH ₃ ⁺ , CH ₂ ⁺ , CH ⁺ , C ⁺	CH ₃ , CH ₂ , CH, C	CH ₄ [*]
C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂ , C ₂	C ₂ H ₆ ⁺ , C ₂ H ₅ ⁺ , C ₂ H ₄ ⁺ , C ₂ H ₃ ⁺ , C ₂ H ₂ ⁺ , C ₂ H ⁺ , C ₂ ⁺	C ₂ H ₅ , C ₂ H ₃ , C ₂ H	C ₂ H ₆ [*] , C ₂ H ₄ [*] , C ₂ H ₂ [*]
C ₃ H ₈ , C ₃ H ₆ , C ₄ H ₂		C ₃ H ₇ , C ₃ H ₅	C ₃ H ₈ [*]
H ₂	H ₃ ⁺ , H ₂ ⁺ , H ⁺ , H ⁻	H	H ₂ [*]
Extra species typically included in CO ₂ /CH ₄ , CO ₂ /H ₂ O, CO ₂ /H ₂ or CH ₄ /O ₂ models			
H ₂ O, H ₂ O ₂	H ₃ O ⁺ , H ₂ O ⁺ , OH ⁺ , OH ⁻	OH, HO ₂	H ₂ O [*]
CH ₂ O, CH ₃ OH, CH ₃ OOH		CHO, CH ₂ OH, CH ₃ O, CH ₃ O ₂	
C ₂ H ₅ OH, C ₂ H ₅ OOH, CH ₃ CHO, CH ₂ CO		CHCO, CH ₃ CO, CH ₂ CHO, C ₂ H ₅ O, C ₂ H ₅ O ₂	
Extra species typically included in CO ₂ /N ₂ and/or CH ₄ /N ₂ models			
N ₂	N ⁺ , N ₂ ⁺ , N ₃ ⁺ , N ₄ ⁺	N	N ₂ (V1-V14), N ₂ (C ³ Π _u), N ₂ (A ³ Σ _u ⁺), N ₂ (α ¹ Σ _u ⁻), N ₂ (B ³ Π _g), N(2D), N(2P)
N ₂ O, N ₂ O ₃ , N ₂ O ₄ , N ₂ O ₅	NO ⁺ , N ₂ O ⁺ , NO ₂ ⁺ , NO ⁻ , N ₂ O ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , N ₂ O ₂ ⁺	NO, NO ₂ , NO ₃	
HCN, ONCN, C ₂ N ₂	HCN ⁺	H ₂ CN, CN, NCO, NCN	
NH ₃	NH ₄ ⁺ , NH ₃ ⁺ , NH ₂ ⁺ , NH ⁺	NH ₂ , NH	NH ₃ [*]
N ₂ H ₄ , N ₂ H ₂		N ₂ H ₃ , N ₂ H	

Table 1.
Overview of the species typically included in plasma chemistry models for pure CO₂, pure CH₄, as well as extra species included in CO₂/CH₄, CO₂/H₂O, CO₂/H₂, and CH₄/O₂ gas mixtures and in CO₂/N₂ or CH₄/N₂ mixtures.

the plasma characteristics vary as a function of distance traveled by the gas, in the same way as they would vary in time in a batch reactor. The time in the balance equations thus corresponds to a residence time of the gas in the reactor, and the time variation can be translated into a spatial variation by means of the gas flow rate.

Besides balance equations for the species densities, 0D chemical kinetic models typically also apply balance equations for the electron temperature and/or the gas temperature, again based on source and loss terms, defined by the power deposition (or electric field) and the chemical reactions. Alternatively, instead of calculating the electron temperature with a balance equation, 0D models often solve a Boltzmann equation (e.g., Bolsig+ [118]), to calculate the electron energy distribution function (EEDF) and the rate coefficients of the electron impact reactions as a

function of the electron energy. A more detailed description of the free electron kinetics in CO₂ plasma is provided in [32–37], where a state-to-state vibrational kinetic model was self-consistently coupled with the time-dependent electron Boltzmann equation.

0D models allow to predict the gas conversion, the product yields, and selectivities, based on the calculated plasma species densities at the beginning and the end of the simulations, corresponding to the inlet and outlet of the plasma reactor. Furthermore, based on the power introduced in the plasma and the gas flow rate, the specific energy input (SEI) can be computed, and from the latter, the energy efficiency (η) can be obtained with the following formulas:

$$SEI \left(\frac{kJ}{l} \right) = \frac{Plasmapower(kW)}{Flowrate \left(\frac{l}{min} \right)} * 60 \left(\frac{s}{min} \right) \quad (2)$$

$$\eta(\%) = \frac{\Delta H_R \left(\frac{kJ}{mol} \right) * X_{CO_2}(\%)}{SEI \left(\frac{kJ}{l} \right) * 22.4 \left(\frac{l}{mol} \right)} \quad (3)$$

where ΔH_R is the reaction enthalpy of the reaction under study (e.g., 279.8 kJ/mol for CO₂ splitting) and X_{CO_2} is the CO₂ conversion. Note that this formula is only applicable to pure CO₂ splitting, but a similar formula can be applied to the other gas mixtures, using another reaction enthalpy and accounting not only for the CO₂ conversion but also for the conversion of the other gases in the mixture.

3.2 2D or 3D fluid modeling

Even though some spatial dependences of the plasma reactors can be taken into account in 0D chemical kinetic models, as explained above, they are not really suitable for describing detailed plasma reactor configuration or predict how modifications to the reactor geometry would give rise to better CO₂ conversion and energy efficiency. For this purpose, 2D or even 3D models are required, and fluid models are then the most logical choice, because they still allow a reasonable calculation time, in contrast to, for instance, PIC-MCC simulations.

These fluid models solve a number of conservation equations for the densities of the various plasma species and for the average electron energy. The energy of the other plasma species can be assumed in thermal equilibrium with the gas. The conservation equations for the species densities are again based on source and loss terms, defined by the chemical reactions, like in the 0D models. The source of the electron energy is due to heating by the electric field, and the energy loss is again dictated by collisions. In addition, transport is now included in the conservation equations, defined by diffusion and by migration in the electric field (for the charged species) and (in some cases) by convection due to the gas velocity. Furthermore, the conservation equations are coupled with Poisson's equation for a self-consistent calculation of the electric field distribution from the charged species densities, although more simplified quasi-neutral (QN) models have also been used [113], to further reduce the calculation time. Such a QN model neglects the near-electrode regions and treats only the quasi-neutral bulk plasma. It does not solve the Poisson equation, but calculates the ambipolar electric field from the ion densities and the electron and ion diffusion coefficients and mobilities.

Finally, in many cases, the gas temperature and gas flow behavior are calculated with a heat transfer equation and the Navier-Stokes equations, respectively, while in GA models, the cathode heat balance can also be accounted for, to properly describe the electron emission processes. The fluid (plasma) model and the models

for gas flow and gas heating are typically combined into a multiphysics model: the calculated gas velocity is inserted in the transport equations of the plasma species, and the gas temperature determines the gas density profile and thus the chemical reaction rates.

4. Some typical calculation results

4.1 0D chemical kinetic modeling

0D chemical kinetic models typically provide information about the calculated gas conversion, energy efficiency, and product formation, as a function of specific operating conditions, as well as about the underlying chemistry explaining these results. The latter will be illustrated here, based on the modeling work performed within our group PLASMANT, for pure CO₂ splitting, as well as CO₂/CH₄, CH₄/O₂, CO₂/H₂, and CO₂/H₂O mixtures. For more details about the modeling results in these mixtures, and more specifically the calculated conversions, product yields and energy efficiencies, and comparison with experiments, we refer to the original research papers mentioned below, as well as two recent review papers [84, 116].

4.1.1 Pure CO₂ splitting

4.1.1.1 DBD conditions

The dominant reaction pathways for CO₂ splitting in a DBD plasma, as predicted from the model in [7], are plotted in **Figure 1**. As a DBD is characterized by relatively highly reduced electric field values (typically above 200 Td), and thus relatively high electron energies (several eV), electron impact reactions with CO₂ ground-state molecules dominate the chemistry. The most important reactions are electron impact dissociation into CO and O (which proceeds through electronically excited CO₂, that is, the so-called electron impact excitation-dissociation), electron impact ionization into CO₂⁺ (which recombines with electrons or O₂⁻ ions into CO and O and/or O₂), and electron dissociative attachment into CO and O⁻ (cf. the thick black arrow lines in **Figure 1**). These three processes account for about 50%, 25%, and 25%, respectively, to the total CO₂ conversion [28]. Because these processes require more energy than strictly needed for breaking the C=O bond (i.e., 5.5 eV), the energy efficiency for CO₂ splitting in a DBD plasma is quite limited, that is, up to maximum 10% for a conversion up to 30% [1].

The CO molecules are relatively stable, but at very long residence time, they will recombine with O⁻ ions or O atoms, to form again CO₂ (cf. thin black arrow lines in **Figure 1**). This explains why the CO₂ conversion typically saturates at long residence times. Furthermore, the O atoms created upon CO₂ splitting also recombine quickly into O₂ or O₃, based on several processes (see also **Figure 1**).

4.1.1.2 MW and GA conditions

While our calculations predict that ca. 94% of the CO₂ splitting in a DBD plasma arises from the ground state, and only ~6% occurs from the vibrationally excited levels [28], the situation is completely different in a MW or GA plasma. These plasmas are characterized by much lower reduced electric field values (in the order of 50–100 Td), creating lower electron energies (order of 1 eV), which are most suitable for vibrational excitation of CO₂. Therefore, the CO₂ splitting in MW and GA discharge is mainly induced by electron impact vibrational excitation of the

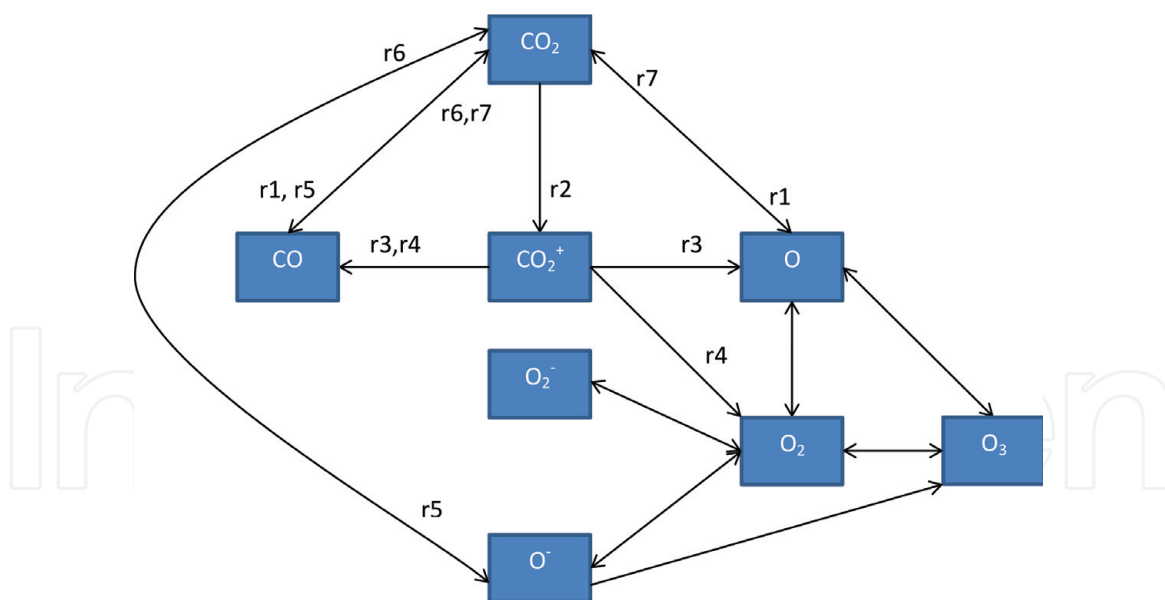


Figure 1.

Dominant reaction pathways of CO_2 splitting and the further reactions between O , O_2 , and O_3 in a DBD plasma, as obtained from the model in [7], where the labels are also explained. Adopted from [119] with permission.

lowest vibrational levels, followed by vibrational-vibrational (VV) collisions, gradually populating the higher vibrational levels, leading to dissociation of CO_2 . This stepwise vibrational excitation, or the so-called ladder climbing, is illustrated in **Figure 2**. As this process only requires 5.5 eV for dissociation, that is, exactly the $\text{C}=\text{O}$ bond energy, this explains why MW and GA discharges exhibit a much better energy efficiency than a DBD, where the dominant dissociation mechanism is electron impact excitation-dissociation, as explained above, which requires 7–10 eV (see **Figure 2**).

Still, it must be realized that the vibrational excitation pathway is not always optimized in a MW or GA plasma. Indeed, as illustrated in detail in [42], the vibrational excitation is higher at lower pressures and higher power densities. The latter give rise to higher electron densities, which yield more vibrational excitation. Higher pressures, on the other hand, result in more vibrational-translational (VT) relaxation collisions, which represent the major loss mechanism of the vibrational energy. Finally, also the gas temperature plays a crucial role, as a higher gas temperature also results in more pronounced VT relaxation. Our models predict that in a MW plasma at atmospheric pressure, the dissociation is too much determined by thermal processes, thus limiting the CO_2 conversion and energy efficiency, in agreement with experimental observations. In addition, the recombination of CO and O atoms also becomes gradually more important at high gas temperature and pressures [42], further explaining why the experimental CO_2 conversion and energy efficiency drop upon increasing pressure. The main processes occurring in a MW plasma in the two extreme cases, that is, the ideal non-equilibrium conditions of low pressure and temperature and high power density and the near-thermal conditions of high pressure and temperature, are summarized in **Figure 3**. The model predicts a much higher CO_2 conversion and energy efficiency in a pressure range of 200–300 mbar and much lower values at atmospheric pressure, in the near-thermal conditions [42]. Hence, we should exploit as much as possible the non-equilibrium character of a MW plasma, in which the higher vibrational levels of CO_2 are overpopulated, to obtain the most energy-efficient CO_2 conversion.

The same conclusions can be drawn for a GA plasma, where our models predict that the CO_2 conversion could be further enhanced, by exploiting the role of the

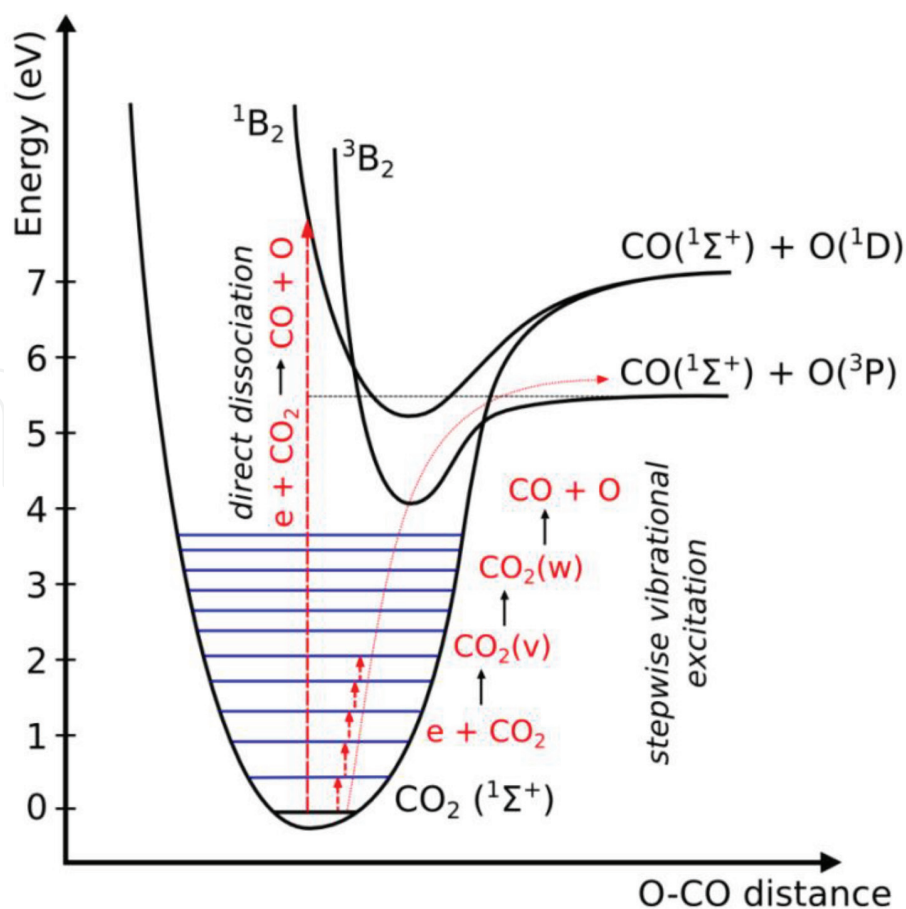


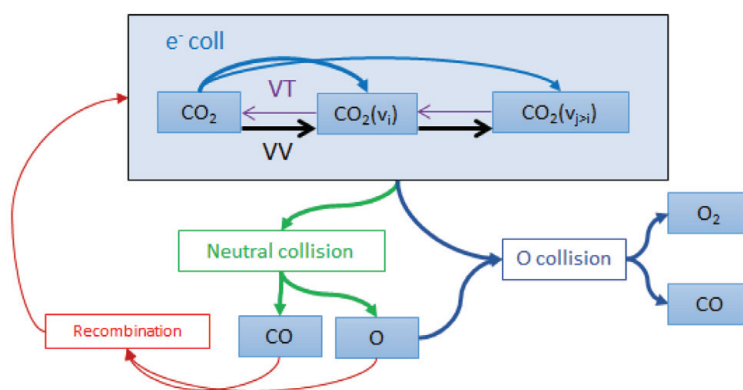
Figure 2. Schematic illustration of some CO₂ electronic and vibrational levels, illustrating the energy-efficient dissociation process through electron impact vibrational excitation, followed by vibrational-vibrational collisions, which gradually populate the higher vibrational levels, that is, the so-called ladder climbing (5.5 eV), compared to direct dissociation through electronic excitation (above 7 eV). Adopted from [119] with permission.

higher vibrational levels of CO₂. Indeed, as the GA operates at atmospheric pressure, the vibrational distribution function (VDF) is too much thermal, that is, there is no significant overpopulation of the higher CO₂ vibrational levels. This was predicted both in a classical GA at a temperature around 1200 K [45] and in a RVF GA, operating at temperatures around 2500–3000 K [47]. The CO₂ dissociation even proceeds mainly from the ground state or the lowest vibrational levels. Indeed, based on these models, the major dissociation process was electron impact dissociation [45] or thermal dissociation [47] of the lower CO₂ vibrational levels, and the chemical reactions of the higher vibrational levels (with either O atoms or any arbitrary molecules in the plasma), which theoretically provide the most energy-efficient process for CO₂ conversion, were found to be of minor importance. Just like in the MW plasma, the model predicts that a significant overpopulation of the VDF, and thus a more energy-efficient CO₂ conversion, can be realized by decreasing the temperature or by increasing the power density [45].

4.1.2 CO₂/CH₄ mixture

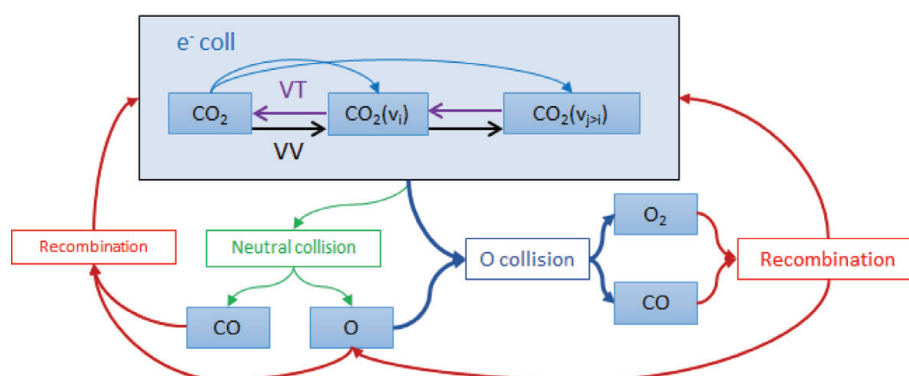
When adding an H-source, such as CH₄, to the CO₂ plasma, a variety of molecules can be formed, with a mixture of H₂ and CO (or syngas) as the major compounds, but also smaller fractions of higher hydrocarbons and oxygenates can be formed. **Figure 4** illustrates the dominant pathways in a CO₂/CH₄ mixture, as predicted by the model in [66]. The thickness of the arrow lines is correlated to the rate of the reaction. CH₄ dissociation is initiated by electron impact, forming CH₃

a)



- High vibrational excitation + VV; low VT
- Dissociation by neutral and O collisions equally important
- Low recombination
- Energy efficient

b)



- Thermal VDF due to high VT
- High recombination
- Energy lost to heat

Figure 3.

Dominant reaction pathways of CO_2 splitting in a MW plasma, as obtained from the model in [42], for two extreme cases: (a) the ideal non-equilibrium conditions of low pressure and temperature and high power density and (b) the near-thermal condition of high pressure and temperature. Adopted from [116] with permission.

radicals, which recombine into higher hydrocarbons. Moreover, electron impact dissociation of CH_4 and of the higher hydrocarbons also yields H_2 formation. In addition, the CH_3 radicals also create methanol (CH_3OH) and CH_3O_2 radicals, albeit to a lower extent. Furthermore, the CH_2 radicals, also created from electron impact dissociation of CH_4 , react with CO_2 to form formaldehyde (CH_2O) and CO . Finally, the O atoms, created from electron impact dissociation of CO_2 (see also **Figure 1**), also initiate the formation of higher oxygenates, like acetaldehyde (CH_3CHO). This species reacts further into CH_3CO radicals and subsequently into ketene (CH_2CO), although these pathways are not so important in absolute terms, as indicated by the thin dashed lines in **Figure 4**.

We have also compared the chemistry in the CO_2/CH_4 mixture, used for dry reforming of methane, with that of partial oxidation of methane, that is, a CH_4/O_2 mixture [66]. The reaction pathways of the latter are depicted in **Figure 5**. The CH_4/O_2 mixture clearly leads to a completely different chemistry than the CO_2/CH_4

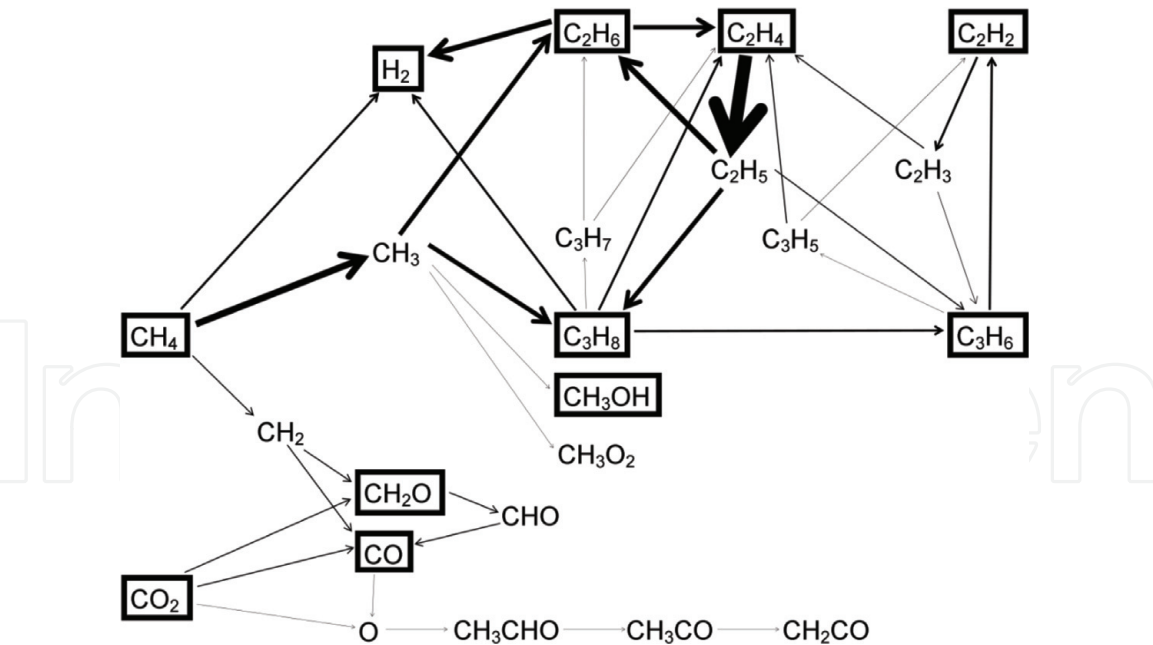


Figure 4.
Dominant reaction pathways for the conversion of CH₄ and CO₂ into higher hydrocarbons, H₂ and CO, and higher oxygenates, in a 70/30 CH₄/CO₂ DBD plasma, as obtained from the model in [66]. The thickness of the arrow lines corresponds to the importance of the reaction paths. Reproduced from [84] with permission.

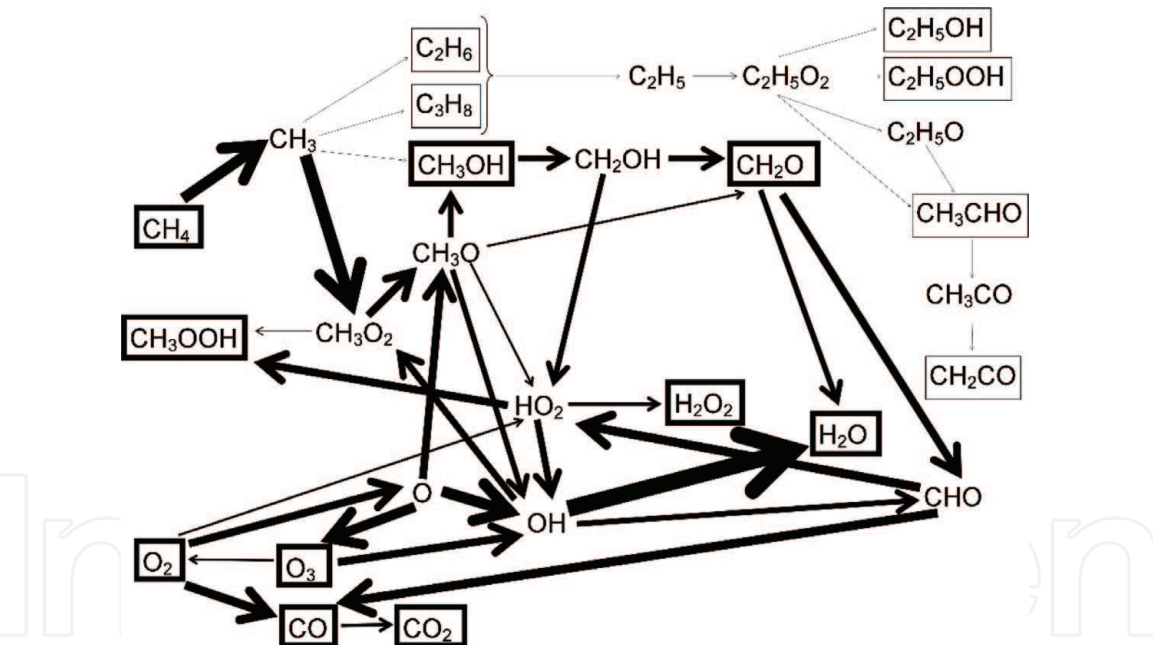


Figure 5.
Dominant reaction pathways for the conversion of CH₄ and O₂ into (mainly) higher oxygenates, as well as some full oxidation products, in a 70/30 CH₄/O₂ DBD plasma, as obtained from the model in [66]. The thickness of the arrow lines corresponds to the importance of the reaction paths. Reproduced from [84] with permission.

mixture, in spite of the fact that the same chemical species are included in the models (see **Table 1**). Electron impact dissociation of CH₄ again produces CH₃ radicals, which will recombine into methanol or higher hydrocarbons, but the recombination into CH₃O₂ radicals, which form either CH₃O radicals or methyl hydroperoxide (CH₃OOH), is now more important. The CH₃O radicals produce methanol, which seems a more important formation mechanism than the recombination of CH₃ with OH radicals (cf. the arrow line thickness in **Figure 5**), and methanol can also react further into CH₂OH radicals, producing formaldehyde. The latter is also easily converted into CHO radicals and further into CO (note the

thickness of these arrow lines, indicating the importance of these reactions) and CO_2 . Furthermore, formaldehyde is also partially converted into H_2O . Note that this pathway is illustrated for a 70/30 CH_4/O_2 mixture, which obviously leads to nearly full oxidation of CH_4 , rather than partial oxidation, where the major end products should be the higher oxygenates. When less O_2 would be present in the mixture, our model predicts that methanol and methyl hydroperoxide are formed in nearly equal amounts as CO and H_2O [66]. **Figure 5** also illustrates that the O_2 molecules are mainly converted into CO , O atoms, and HO_2 radicals. Some O_3 is also formed out of O_2 , but the reverse process, that is, the production of two O_2 molecules out of O_3 and O atoms, is more important, explaining why the arrow points from O_3 toward O_2 . The O atoms are converted into CH_3O and OH radicals, producing methanol and water, respectively. The latter reaction (from OH to H_2O) appears to be very important (cf. thick arrow line in **Figure 5**), and thus, significant amounts of H_2O are formed, as predicted by the model [66].

In summary, comparing **Figures 4** and **5** clearly indicates that the chemical pathways in CH_4/O_2 and CH_4/CO_2 plasma are quite different, even at the same mixing ratios. Finally, in both mixtures a large number of different chemical compounds can be formed, but due to the reactivity of the plasma, there is no selective production of some targeted compounds. To reach the latter, the plasma will have to be combined with a catalyst.

4.1.3 CO₂/H₂ mixture

The dominant reaction pathways for the conversion of CO_2 and H_2 in a 50/50 CO_2/H_2 DBD plasma are illustrated in **Figure 6**, as predicted by the model in [75]. The conversion starts again with electron impact dissociation of CO_2 , yielding CO and O atoms. Simultaneously, electron impact dissociation of H_2 results in the formation of H atoms, and this reaction seems more important (cf. the thickness of the arrow line). The O and H atoms recombine into the formation of OH radicals and further into H_2O . The model thus predicts that H_2O is produced at relatively high density [75]. The CO molecules will partially react back into CO_2 , mainly through the formation of CHO radicals. This pathway appears to be more important than the direct three-body recombination between CO and O atoms into CO_2 , which is the dominant pathway in a pure CO_2 plasma. The H atoms thus contribute

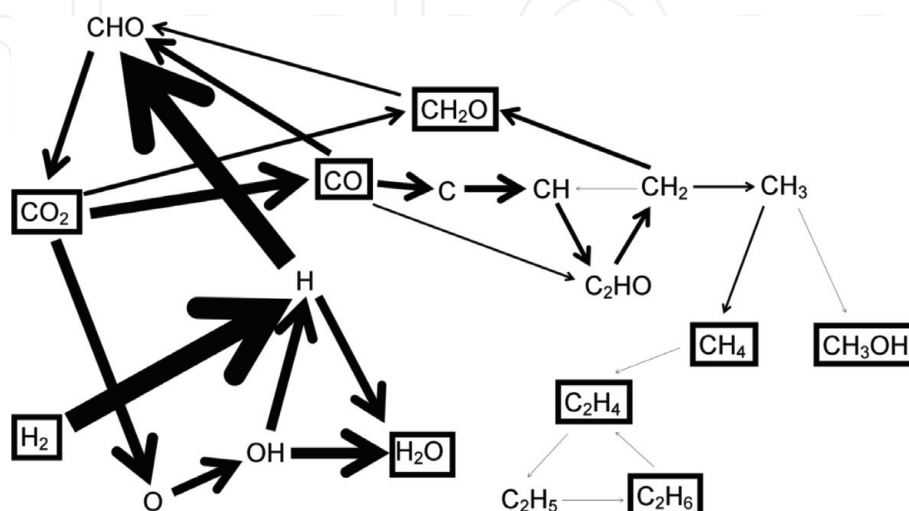


Figure 6. Dominant reaction pathways for the conversion of CO_2 and H_2 into various products, in a 50/50 CO_2/H_2 DBD plasma, as obtained from the model in [75]. The thickness of the arrow lines corresponds to the rates of the net reactions. The stable molecules are indicated with black rectangles. Reproduced from [75] with permission.

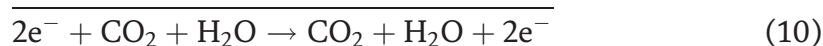
significantly to the back reaction of CO into CO₂, and this explains why the calculated CO₂ conversion is quite limited in a CO₂/H₂ mixture [75]. Electron impact dissociation of CO yields the formation of C atoms, which react further into CH, CH₂, C₂HO, and CH₃ radicals in several successive radical recombination reactions. The CH₂ radicals react with CO₂ into CH₂O, while the CH₃ radicals easily form CH₄. The latter reaction is more favorable than CH₃OH formation out of CH₃. Finally, CH₄ partially reacts further into higher hydrocarbons (C_xH_y).

Figure 6 clearly illustrates that several subsequent radical reactions are required for the formation of (higher) hydrocarbons and oxygenates. This explains the very low calculated yields and selectivities of these end products [75]. In summary, the lack of direct formation of CH₂ and CH₃ in the CO₂/H₂ mixture, which is important in CO₂/CH₄ gas mixtures (see **Figure 4**), combined with the very low conversion of CO₂, which is again attributed to the absence of CH₂ as important collision partner for the loss of CO₂, makes the CO₂/H₂ mixture less interesting for the formation of higher hydrocarbons and oxygenates than a CO₂/CH₄ mixture at the conditions under study. Furthermore, as H₂ is a useful product by itself, while CH₄ is also a greenhouse gas (besides a fuel), the simultaneous conversion of CO₂ and CH₄, that is, two greenhouse gases, is considered to be of higher value, also because it represents a direct valorization of biogas.

4.1.4 CO₂/H₂O mixture

H₂O is the cheapest H-source to be added to a CO₂ plasma for the direct production of value-added chemicals, and the combined conversion of CO₂ and H₂O could mimic the natural photosynthesis process. However, adding H₂O (in concentrations up to 8%) to a CO₂ DBD plasma causes a significant reduction in the CO₂ conversion, while no oxygenated hydrocarbons were detected experimentally, and also the calculated concentrations were only in the ppb level [73].

These results can be explained by a kinetic analysis of the reaction chemistry. The latter reveals that the reaction between CO and OH, yielding H atoms and CO₂, is crucial, as it has a very high rate constant, and it controls the ratio between the conversions of CO₂ and H₂O. This can be explained in a very simple way by the following reactions:



Reactions (4) and (5) yield the dissociation of CO₂ and H₂O, but the products, CO and OH, will rapidly recombine into CO₂ again (reaction (6)). Moreover, the two H atoms and one O atom formed will also quickly recombine, first into OH (through subsequent reactions (7) and (8)) and subsequently into H₂O through reaction (9). Thus, overall, there is no net dissociation of CO₂ and H₂O in this pathway (see overall reaction (10)).

Of course, there exist also other pathways for the conversion of these molecules, so there will still be some conversion of CO₂ and H₂O in the plasma, but electron

impact dissociation is typically the major loss mechanism for CO_2 in a DBD (cf. also above), so the above mechanism explains the drop in CO_2 conversion upon addition of H_2O , as the OH radicals created upon H_2O dissociation give rise to the back reaction, creating CO_2 out of CO.

The above mechanism can also explain why no (significant) methanol (or other oxygenated hydrocarbons) is formed in the $\text{CO}_2/\text{H}_2\text{O}$ mixture, because all the H atoms needed to form CH and CHO fragments for the formation of methanol are steered to OH and subsequently H_2O again. Hence, this chemical kinetic analysis indicates that H_2O might not be a suitable H-source for the formation of oxygenated hydrocarbons in a one-step process, because of the abundance of O atoms, O_2 molecules, and OH radicals, trapping the H atoms.

It should be noted that this fast reaction between H and O atoms was demonstrated to be useful for the O-trapping in the case of pure CO_2 conversion, thus providing a solution for the separation of the CO_2 splitting products [120], but in the present case, it is clearly the limiting factor for the formation of oxygenated hydrocarbons.

4.1.5 CO_2/N_2 mixture

Real industrial gas flows typically do not contain pure CO_2 but also other gases and impurities. In most cases, N_2 is the most important component. It is thus also important to study the effect of N_2 on the CO_2 conversion and energy efficiency, as well as which products are formed, that is, useful products or harmful NO_x compounds. Hence, we developed some models for a CO_2/N_2 mixture, both for a MW plasma [76] and a DBD [77]. Both models predict that N_2 has a beneficial effect on the CO_2 splitting, but the mechanism is completely different. In a DBD, the electronically excited metastable $\text{N}_2(\text{A}^3\Sigma_u^+)$ molecules give rise to the enhanced CO_2 splitting [77], while in a MW plasma, the N_2 vibrational levels help to populate the CO_2 vibrational levels, by VV relaxation, and this causes the enhanced CO_2 splitting [76]. It should be mentioned, however, that in spite of the higher absolute CO_2 conversion upon addition of N_2 , the effective or overall CO_2 conversion will drop in both cases, because of the lower absolute fraction of CO_2 in the gas mixture. The effect is minor up to about 60% N_2 but more pronounced for higher N_2 fractions. As the effective CO_2 conversion determines the overall energy efficiency of the process, the latter also drops upon addition of more N_2 , as some of the energy is used for ionization, excitation, and dissociation of the N_2 molecules.

Both the modeling and experiments also reveal that several NO_x compounds are produced in a CO_2/N_2 plasma, especially NO, NO_2 , N_2O , and N_2O_5 , as was discussed in detail in [77]. A detailed chemical kinetic analysis reveals how the NO_x compounds are formed and thus also how this formation can be reduced. As illustrated in **Figure 7**, N_2 is excited to a metastable state $\text{N}_2(\text{A}^3\Sigma_u^+)$, as well as dissociated into N atoms, by electron impact reactions. The $\text{N}_2(\text{A}^3\Sigma_u^+)$ molecules react with O atoms into NO or with O_2 into N_2O . The N atoms react with both O and O_3 into NO. NO can be converted into NO_2 upon reaction with O, but the opposite reaction, upon collision with either O or N atoms, occurs as well, making NO_2 the main source of NO production and vice versa (see **Figure 7**).

Furthermore, the N atoms are trapped in two reaction loops, that is, between NO, NO_2 , and N_2O_3 and between NO_2 , NO_3 , and N_2O_5 . The only way to escape from these loops is by the reaction of NO_2 to N_2O (which can react back to N_2 and N upon collision with $\text{N}_2(\text{A}^3\Sigma_u^+)$ and N_2^+) or by the reaction of NO with either N atoms or $\text{N}_2(\text{a}^1\Sigma_u^-)$ molecules, forming again N atoms or N_2 molecules (see **Figure 7**).

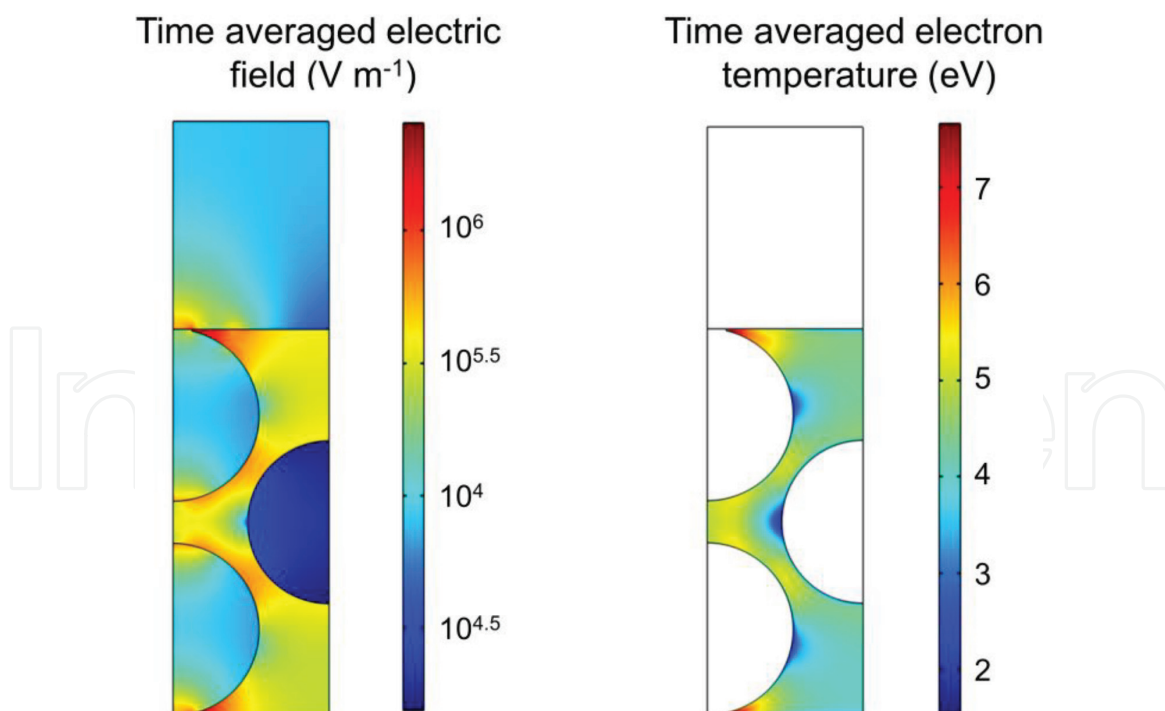


Figure 8.

Calculated time-averaged 2D profiles of the electric field and electron temperature in a packed bed DBD reactor, at a peak-to-peak voltage of 4 kV and a frequency of 23.5 kHz, as obtained from the model in [94]. Adopted from [94] with permission.

more pronounced in a so-called “contact point” model (see [94]). This enhanced electric field gives rise to more electron heating and thus to a higher electron temperature in between the beads (see right panel of **Figure 8**). At this relatively low applied voltage of 4 kV, the plasma is initiated at the contact points and remains in this region, reflecting the properties of a Townsend discharge, while at higher applied voltage, for example, 7.5 kV (peak-to-peak), the discharge will spread out more into the bulk of the reactor, from one void space to the other, ultimately covering the whole gas gap [94]. Such behavior was also reported from experiments. Indeed, by means of an intensified charge-coupled device (ICCD) camera [121, 122], Kim and coworkers also observed that at low applied potential, the discharge stays local at the contact points, while at higher potential, it spreads across the surface of the packing material, and similar observations were also made by Tu et al. [123].

Although the above model was developed for helium, we expect a similar behavior in a CO₂ plasma. The higher electron temperature will give rise to more electron impact ionization, excitation, and dissociation of the CO₂ molecules, for the same applied power, and this can explain why a packed bed DBD gives a higher CO₂ conversion and energy efficiency than an empty reactor.

We also developed a model for a packed bed DBD reactor in dry air, to study the propagation of a plasma streamer [97], as illustrated in **Figures 9 and 10**. Our calculations reveal that the plasma formation in a packed bed DBD reactor in dry air may exhibit three types of discharge behavior, that is, positive restrikes; filamentary microdischarges, also localized between the packing beads; and surface ionization waves, in agreement with the model by Kruszelnicki et al. [93]. Positive restrikes between the dielectrics result in the formation of filamentary microdischarges. Surface charging creates electric field components parallel to the dielectric surface and leads to the formation of surface ionization waves. At a low dielectric constant of the packing ($\epsilon_r = 5$), plasma ignition between the beads occurs

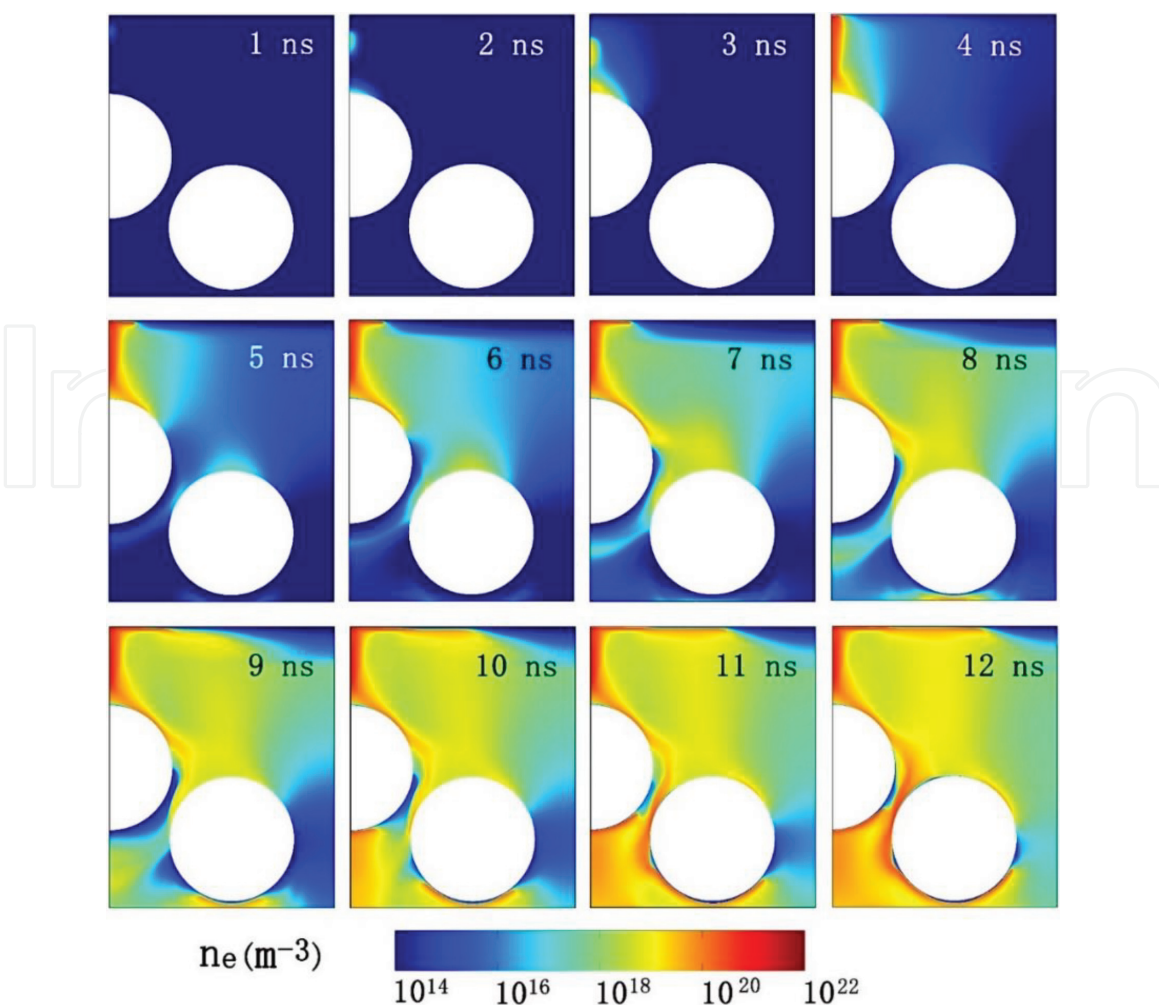


Figure 9.
 Calculated electron number density distribution as a function of time, for a packed bed DBD reactor in dry air, with packing beads of $\epsilon_r = 5$. Adopted from [97] with permission.

directly in the mode of surface discharges (or surface ionization waves), which can connect with the surface of the adjacent bead; see **Figure 9**. On the other hand, at high dielectric constants ($\epsilon_r = 1000$), no surface streamer jumping toward the adjacent bead surface is observed, and spatially limited filamentary microdischarges, so-called local discharges, are generated between the beads; see **Figure 10**. For intermediate dielectric constants, a mixed mode of surface discharges and local discharges exists [97]. Good qualitative agreement with experiments was obtained, as detailed in [97].

The positive restrikes, local discharges, and surface discharges all give rise to the production of reactive species, because they exhibit an enhanced electric field and thus they create a burst of energetic electrons, which produce reactive species by electron impact dissociation. Packed bed reactors are often used for plasma catalysis, where packing beads with different dielectric constants can act as supports for the catalytic materials. Therefore, this study is important to gain a better insight on how different packing materials can influence the performance of packed bed DBD reactors for plasma catalysis. As our results indicate that a higher dielectric constant constrains the discharge to the contact points of the beads, this may limit the catalyst activation due to the limited catalyst surface area in contact with the discharge, and thus it may have implications for the efficiency of plasma catalytic CO₂ conversion. Indeed, the best results are not always reached for the highest dielectric constant [9, 10].

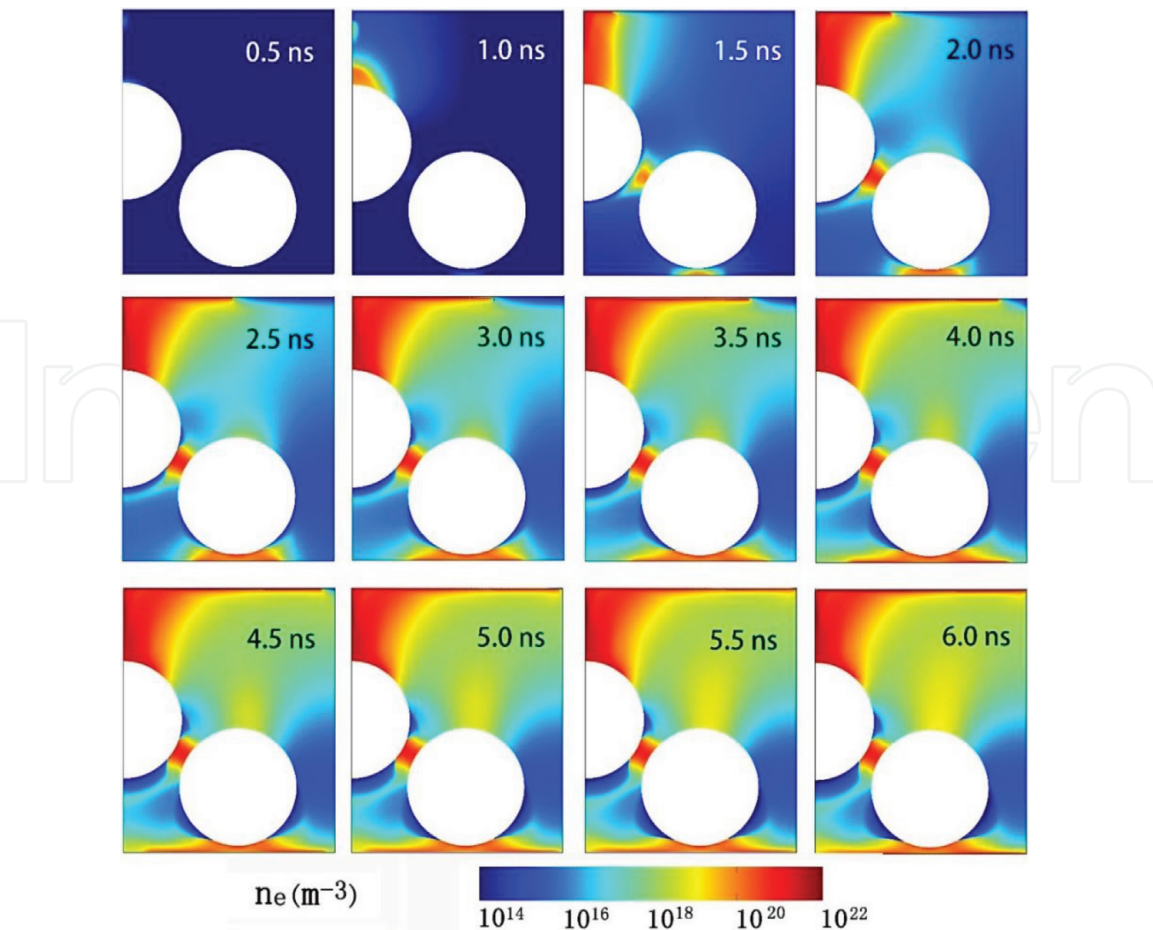


Figure 10. Calculated electron number density distribution as a function of time, for a packed bed DBD reactor in dry air, with packing beads of $\epsilon_r = 1000$. Adopted from [97] with permission.

4.2.2 Gliding arc plasmatron (GAP)

Figure 11 illustrates a typical 3D gas flow pattern (a), as well as the calculated electron density profile (b), in a reverse vortex flow (RVF) GA plasma reactor, also called gliding arc plasmatron (GAP), operating in argon. The stream line plot clearly

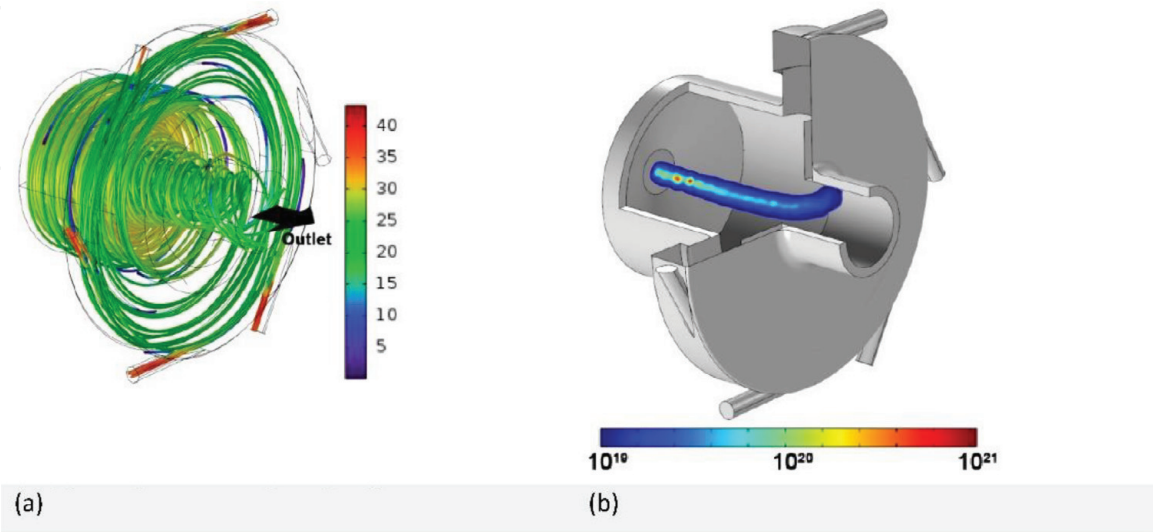


Figure 11. Calculated steady-state gas flow stream lines (a) and electron density at a time of 5.3 ms, when the arc is stabilized in the center (b), for a reverse vortex flow GA plasma reactor at an arc current of 240 mA, as obtained from the model in [87].

depicts the formation of a reverse vortex flow. The gas is forced into a tangential motion due to the tangential inlets and travels in this way, close to the sidewalls, toward the closed cathode side at the end (= back of **Figure 11(a)**) with a velocity around 30–40 m/s. After it has reached the closed cathode end, it moves in the opposite direction, in a smaller inner (reverse) vortex toward the outlet, with much lower velocity, and it exits the reactor with a velocity around 20 m/s (see also the color scale in **Figure 11(a)**).

The arc plasma reacts to this gas flow pattern, in the sense that when the gas stream is forced to the center, the arc channel will also move to the center (due to convection), and it will stay in this position as long as the gas keeps it stabilized. Hence, the arc plasma is effectively stabilized in the center, as illustrated in **Figure 11(b)**. Furthermore, as the mass transfer is directed toward the center, the walls are thermally insulated from the hot plasma arc column. The fact that no heat is lost to the reactor walls or other parts of the reactor means that more power can be consumed by the discharge, that is, the plasma generation is more effective. Furthermore, keeping the walls insulated (cold) is also beneficial for the reactor materials itself. The calculated plasma density, for an arc current of 240 mA, is around 10^{20} m^{-3} , which is a typical value for GA plasmas at atmospheric pressure.

It should be noted that the results of **Figure 11** are for an argon plasma, but we also developed a similar model for a CO₂ plasma, but this was only possible in 2D, because of computation time [87]. However, in the same paper, we also “downgraded” the 3D argon model into 2D, and a comparison between both indicated that the difference between the 3D and 2D argon models was limited. Therefore, the 2D CO₂ model provides data with reasonable accuracy. We calculated a typical plasma density of $4 \times 10^{19} \text{ m}^{-3}$ in the arc center, which is about one order of magnitude lower than in argon ($4 \times 10^{20} \text{ m}^{-3}$), due to other chemical processes, not all leading to ionization.

We can conclude from **Figure 11** that the gas, when moving in the inner vortex flow will largely pass through the arc column. This result is very interesting for the application of CO₂ conversion, as it shows that the design of this GAP allows more gas to pass through the arc zone than in a classical (diverging electrodes) GA. Nevertheless, our combined simulations and experiments reveal that the fraction of gas that passes through the arc is still somewhat limited, thus limiting the overall CO₂ conversion [19, 20]. By means of this type of 3D fluid dynamics modeling, we aim to predict a more optimized design, to further improve the application of CO₂ conversion.

5. Conclusion

Plasma-based CO₂ conversion is gaining increasing interest, but to improve this application, we need to obtain a better insight in the underlying mechanisms. The latter can be obtained by both plasma chemistry modeling and plasma reactor modeling. This chapter shows some examples of both modeling approaches from our own group, to illustrate what type of information can be obtained from such models and how this modeling can contribute to a better insight, in order to improve this application.

0D chemical reaction kinetic modeling is very suitable for describing the underlying plasma chemical reaction pathways of the conversion process. We have illustrated this for pure CO₂ splitting, showing the difference between a DBD and MW/GA plasma. Indeed, in a DBD, the CO₂ conversion is mainly due to electron impact electronic excitation followed by dissociation with the CO₂ ground-state molecules,

which requires about 7–10 eV per molecule. This “waste of energy” explains the lower energy efficiency of CO₂ splitting in a DBD. On the other hand, in a MW and GA plasma, vibrational excitation of CO₂ is dominant, and VV relaxation gradually populates the higher vibrational levels (so-called ladder climbing). This is the most energy-efficient way of CO₂ dissociation, as it requires only 5.5 eV per molecule, that is, exactly the C=O bond energy.

We also presented the important reaction pathways in CO₂/CH₄, CH₄/O₂, CO₂/H₂ and CO₂/H₂O mixtures, as well as for the effect of N₂ addition to a CO₂ plasma. In a DBD plasma, the conversion is always initiated by electron impact dissociation, creating radicals that react further into value-added compounds. The main products formed are syngas (CO/H₂), but higher hydrocarbons and oxygenates are also formed in limited amounts. However, the selective production of these targeted compounds is not yet possible, due to the high reactivity of the plasma. Therefore, a catalyst must be inserted in the plasma. Our models reveal that CO₂/CH₄ and CH₄/O₂ mixtures exhibit totally different chemical reactions, resulting in different products. A CO₂/H₂ mixture does not produce many higher hydrocarbons and oxygenates, and the CO₂ conversion is very limited, due to the lack of CH₂ (and CH₃) radical formation. Indeed, the CH₂ radicals are the main collision partners of CO₂ in the CO₂/CH₄ mixture. Furthermore, adding H₂O to a CO₂ DBD plasma yields a drop in CO₂ conversion, and also the H₂O conversion is limited, and virtually no oxygenated hydrocarbons are formed, which could also be explained from the chemical reaction paths. The insights obtained by the model might be useful to provide possible solutions. The last example of 0D chemical kinetic modeling was given for a CO₂/N₂ plasma, where it was shown that also NO_x compounds are produced, which might give several environmental problems. Again, the model can explain their formation, which is useful to provide possible solutions on how to avoid this NO_x formation.

Although 0D models can give useful information on the plasma chemistry, they cannot really account for details in the plasma reactor configuration and thus predict how modifications to the reactor design might lead to improved CO₂ conversion. For this purpose, 2D or 3D fluid models of specific reactor designs are needed. Developing such fluid models for a detailed plasma chemistry, however, leads to excessive calculation times. Therefore, these models are up to now mainly developed for simpler chemistry, in argon or helium. We have shown here examples for a packed bed DBD reactor and a GAP. These models allow to elucidate why certain reactor designs give beneficial results and to pinpoint the limitations and finally how improvements in the reactor designs might yield a better CO₂ conversion and energy efficiency.

In the future work, we intend to implement the more complex CO₂ chemistry (either pure or mixed with other gases) in such fluid models, to obtain a more comprehensive picture of CO₂ conversion in a real plasma reactor geometry. As this is quite challenging in terms of computation time, reduced chemistry sets must be developed for CO₂ and its gas mixtures. When modeling CO₂ conversion in a MW or GA plasma, the vibrational kinetics must be accounted for. To avoid the need of describing all individual levels, we have developed a level-lumping strategy [39], which enables to group the vibrational levels of the asymmetric stretch mode of CO₂ into a number of groups. This reduces the calculation time, so that it can be implemented in 2D models [86]. We believe that a combination of 0D chemical kinetic models (to obtain detailed insight in the entire plasma chemistry and to develop reduced chemistry sets, identifying the main species and chemical reactions) and 2D/3D fluid models (for a detailed understanding of the reactor design) is the most promising approach to make further progress in this field.

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