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Pinpointing energy losses in CO_2 plasmas – Effect on CO_2 conversion

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ABSTRACT

Plasma technology is gaining increasing interest for CO_2 conversion, but to maximize the energy efficiency, it is important to track the different energy transfers taking place in the plasma. In this paper, we study these mechanisms by a 0D chemical kinetics model, including the vibrational kinetics, for different conditions of reduced electric field, gas temperature and ionization degree, at a pressure of 100 mbar. Our model predicts a maximum conversion and energy efficiency of 32% and 47%, respectively, at conditions that are particularly beneficial for energy efficient CO_2 conversion, i.e. a low reduced electric field (10 Td) and a low gas temperature (300 K). We study the effect of the efficiency by which the vibrational energy is used to dissociate CO_2, as well as of the activation energy of the reaction $CO_2 + O \rightarrow CO + O_2$, to elucidate the theoretical limitations to the energy efficiency. Our model reveals that these parameters are mainly responsible for the limitations in the energy efficiency. By varying these parameters, we can reach a maximum conversion and energy efficiency of 86%. Finally, we derive an empirical formula to estimate the maximum possible energy efficiency that can be reached under the assumptions of the model.

1. Introduction

Since the beginning of the industrial revolution, a large part of the world's energy production is based on processes involving the combustion of fossil fuels. These processes release the carbon contained in the fuels into the atmosphere in the form of CO_2, thus giving rise to an alarming increase of the atmospheric CO_2 concentration. It is now widely accepted that the anthropogenic CO_2 emissions are responsible for the increase of the surface temperature on Earth [1]. Hence, there is a growing interest into various methods to find alternative, renewable energy sources. These energy sources typically have an important drawback: the intermittency of their power generation. Therefore, over the last few years, large research efforts have been directed towards finding solutions for energy storage. One of these methods, the conversion of CO_2 into value-added compounds, has recently received a great interest [2–4]. For instance, the conversion of CO_2 to CO (and oxygen), followed by conversion into hydrocarbons through the Fischer–Tropsch process, would be an interesting way to store energy via a carbon-neutral process. Plasma technology could be suitable for this process, because it uses electricity, and can easily be switched on/off, thus allowing to store intermittent electrical energy. It was indeed shown that low-temperature non-equilibrium plasmas can be an energy-efficient way to dissociate CO_2 [5,2]. In such plasmas, the electrons acquire a much higher temperature than the heavy particles (e.g. the gas molecules), so they can activate the gas by electron impact excitation, ionization and dissociation, without the need to heat the entire gas. This enables endothermic reactions to occur at low temperature, thus keeping the energy cost lower than in a thermal process [5]. This is naturally an interesting property in the framework of energy storage.

The most common types of discharges studied for CO_2 conversion are microwave (MW) plasmas [6–10], gliding arc (GA) plasmas [11–13] and dielectric barrier discharges (DBD) [14–17], although other plasma types are being investigated as well, such as ns-pulsed discharges [18,19], spark discharges [20] and atmospheric glow discharges [21].

While MW and GA plasmas offer relatively high energy efficiencies in most lab-experiments, the energy efficiency of DBDs remains rather low. One the main differences between MW and GA plasmas on the one hand, and DBDs on the other hand, is the value of the electron temperature, which tends to be higher in a DBD [22]. This electron temperature results from the reduced electric field (i.e. electric field divided by gas density), which is indeed higher in a DBD than in a MW and GA plasma [2,23].

The commonly accepted explanation to this lower energy efficiency in a DBD is that a higher electron temperature favors dissociation of CO_2 by direct electron impact from the ground state. This process requires more energy than strictly needed for dissociation, as it results in the creation of electronically excited O atoms. On the other hand, at low electron temperature, characteristic for MW and GA plasmas, it would be possible, through electron impact vibrational excitation and

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vibrational pumping, to climb the vibrational energy ladder of CO_2, until the dissociation energy is reached, which is much more energy efficient [2,5,22–24]. This phenomena is also described in other gases, such as H_2, N_2 and CO [25].

Evidence shows, however, that both MW and GA plasmas, in most experiments, especially at atmospheric pressure, are in close-to thermal equilibrium [10,26,27,13]. Indeed, the vibrational distribution function (VDF) follows a Boltzmann distribution, and is thus not overpopulated at the highest levels, needed for efficient dissociation. Thus, MW and GA plasmas at atmospheric pressure are not taking full advantage of the possibilities offered by non-equilibrium, that are characteristic for plasma.

Over the last few years, the research on CO_2 plasma kinetics modeling has been focusing on finding ways to enhance the energy efficiency of the CO_2 plasma by achieving a better understanding of the underlying processes leading to dissociation, and in particular vibrational excitation.

Pietanza and coworkers [28–33] focused on the coupling between the electron energy distribution function (EEDF) and the CO_2 plasma kinetics, as well as the different dissociation mechanisms. Recently, they further investigated the CO kinetics in a state-to-state model [34]. In our group, we have focused on the key role of vibrational excitation in a CO_2 plasma and its influence on the plasma kinetics and energy efficiency of CO_2 conversion in MW and GA plasma vs DBDs [22,26,27,35–39].

Furthermore, Ponduri et al. [40] developed a time-dependent 1D model to describe the conversion of CO_2 in a DBD. Grofulović et al. [41] proposed a new set of cross sections for CO_2 plasmas. This set was validated from the comparison between swarm data obtained by solving Boltzmann equation and available experimental data. The role of the electron impact dissociation cross-section was further investigated in our group [42].

More recently, following the method of Turner [43–45], and in continuation of the work of Koelman et al. [46] on the verification of the rate coefficients used in our CO_2 kinetics model, we have also investigated how the uncertainties present on the measurements of the rate coefficients can affect the outputs of the model [47]. We have found that the uncertainty on certain important calculation results, such as the CO_2 conversion, can reach up to 100%. However, this study also revealed that the trends predicted by the model are typically not very affected by the uncertainty on the rate coefficient data, implying that this type of modeling should focus on trends rather than on absolute values.

In the present work, we investigate, using a 0D chemical kinetics model, the way in which energy transfers take place inside the plasma. Indeed, energy efficiencies reported for plasma-driven CO_2 conversion reach up to 90% for a MW plasma operating with a supersonic flow [5,6], where the plasma is formed in the low pressure zone of the flow. Modeling, on the other hand, has only reached energy efficiencies in the vicinity of 30% at best [22,26]. The record energy efficiencies of the early experiments carried out in the former Soviet Union [5,6] have not been reproduced since then. However, energy efficiencies reaching up to 48% have been reported in experiments carried out recently at DIFFER [9]. Therefore, we want to check which energy losses might be present in the model, and/or which processes limit the theoretical energy efficiency. This should allow us to understand the limitations to energy efficient CO_2 conversion, both in the model and in general.

Therefore, we use conditions that were found to be ideal for CO_2 conversion in our previous work [26]. In continuation of our work on the uncertainties of the rate coefficients, we investigate here also the effect of the parameters chosen in the scaling laws on dissociation reaction rate coefficients, as well as the effect of the activation energy of the reaction $CO_2 + O \rightarrow CO + O_2$, as these two parameters are expected to limit the energy efficiency of CO_2 conversion.

Furthermore, to investigate the effect of different plasma operating conditions on energy efficient CO_2 conversion, we also consider different values of the reduced electric field, as well as different gas temperatures and different ionization degrees. These correspond to the parameters that can be improved by optimizing the design of the discharge setup. Some of these conditions might be difficult to currently reproduce experimentally, but can be considered as recommendations towards future experiments.

The paper is organized as follows. In Section 2, the model is described, as well as the chemistry set considered. The results are shown in Section 3. In Section 3.1, the CO_2 conversion and energy pathways are analyzed for different conditions of reduced electric field, gas temperature and ionization degree. Section 3.2 is dedicated to the verification of the rate coefficients and scaling laws used for the two main neutral dissociation reactions, to elucidate their effect on the calculated CO_2 conversion and energy efficiency. Section 3.3 attempts to define a general expression for the maximum energy efficiency that can be obtained with plasma. Finally, conclusions are given in Section 4.

2. Model description

2.1. Chemistry set

Table 1 lists the species taken into account in this work. The chemistry set considered here is the same as in our previous work, following kinetic data literature verification [47]. A rather small set is used here, compared to the model of Refs. [36,22,26], because these species and reactions are found to play the dominant role, and adding more (minor) species and (minor) reactions increases the uncertainty on the results and does not lead to a better accuracy, while increasing computation time.

The model takes into account the asymmetric mode vibrational levels of CO_2 up to the dissociation limit, as well the first 4 symmetric mode vibrational levels and the first 10 vibrational levels of CO. It was found in our previous research [37] that the higher vibrational levels of CO do not make a significant difference to the models result.

The list of reactions included in the model is shown in Appendix A. Tables A.1 and A.2 present the list of electron impact reactions

Table 1
Species described in the model.

Neutral ground states	CO_2	CO	O_2	O	$C_{(g)}$
Standard formation enthalpy [48] [eV]	−4.08	−1.15	0	2.58	7.43

Charged species
CO_2^+, CO^+, CO_4^+, O^-, O_2^-, CO_3^-, CO_4^-, e^-

Excited states	Associated energy [eV]	State[a]
$O_2[v_{1-4}]$	Anharmonic oscillator	
$CO[v_{1-10}]$	Anharmonic oscillator	
$CO_2[v_{1-21}]$	Anharmonic oscillator	(00n)
$CO_2[v_a]$	0.083	(010)
$CO_2[v_b]$	0.167	(020) + (100)
$CO_2[v_c]$	0.252	(030) + (110)
$CO_2[v_d]$	0.339	(040) + (120) + (200)
$CO_2[e_1]$	10.5	$(^1\Sigma_u^+)$ + $(^3\Pi_u)$ + $(^1\Pi_u)$
$O_2[e_1]$	0.98	$(a^1\Delta_g)$ + $(b^1\Sigma_g^+)$
$O_2[e_2]$	8.4	$(B^3\Sigma_u^-)$ + higher triplet states
$CO[e_1]$	6.22	$(a^3\Pi_r)$
$CO[e_2]$	7.9	$(A^1\Pi)$
$CO[e_3]$	13.5	$(a'^3\Sigma^+)$ + $(d^3\Delta_i)$ + $(e^3\Sigma^-)$ + $(b^3\Sigma^+)$
$CO[e_4]$	10.01	$(C^1\Sigma^+)$ + $(E^1\Pi)$ + $(B^1\Sigma^+)$ + $(I^1\Sigma^-)$ + $(D^1\Delta)$

[a] CO_2 electronic states designation from Grofulović et al. [41], O_2 and CO electronic states notation from Huber and Herzberg [49].