

Plasma-based Recycling of Carbon Dioxide

Seren Coşkun*

**University of Lisbon, Instituto Superior Técnico, Department of Energy Engineering and Management*

Avenida Rovisco Pais, 1049-001 Lisbon, Portugal. July 2015.

ABSTRACT

CO₂ gas emissions arising from combustion of fossil fuels and the industrial activities have become more of a concern on a global scale. In this thesis, a closed-loop cycle is proposed for recycling the CO₂ and transforming it into something useful, such as hydrocarbon fuels or alcohols. All intermediate steps of this “Carbon Capture and Recycle” process are examined. Among these steps, for conversion of CO₂ into CO, the focus is given to non-thermal plasmas under non-equilibrium conditions.

When compared to conventional dissociation methods, non-thermal plasmas can initiate the process with lower energy, due to collisions that entail subsequent energy transfers. Another advantage of non-thermal laboratory plasmas is that they can be started with renewable energies when the energy is not in demand, making the cycle carbon neutral.

A numerical model is built to simulate CO₂ dissociation in non-thermal plasmas. Effects of three vibrational reactions of energy transfer (e-V, V-T, V-V) are examined and process parameters are altered in order to obtain comparative results. It is shown that it is possible to achieve an effective dissociation process under some specific operation conditions. Gas temperature is found to have a crucial impact on the overall process since increasing temperatures increase the V-T relaxation effect. On the other hand, the gas temperature difference between the discharge and afterglow phases promotes the V-V pumping up. The competition between V-T and V-V energy exchanges is observed from the obtained results.

Keywords: Sustainable fuel, CO₂ recycling, CO₂ dissociation, non-equilibrium, plasma, microwave discharge

1. Introduction

Carbon dioxide (CO₂) emissions released to the atmosphere and arising from industrial activities, as well as power production from the combustion of fossil-based fuels have become more of a concern as a result of their growing scale in the past decades. More than half of aggregate fossil-fuel consumption has been recorded since 1980 and overbalanced in the most recent years. The inclining concentration of CO₂ gas along with other greenhouse gases, have then been unfavorably affecting the ecosystem and therefore the human society (Andres et al., 2012).

An essential step to be taken is clearly the limitations regarding CO₂ production and release. It is also important to find alternative ways of reducing CO₂ emissions if not to cut them completely in the short run. For this reason, a new approach has emerged within the frame of “Carbon Capture and Recycle” (Boretti, 2013; Goede et al., 2014; Goeppert, Czaun, Jones, Surya Prakash, & Olah, 2014; Olah, Prakash, & Goeppert, 2011). This novel approach (Figure 1) indicates a cycle starting from the carbon capture process from the industry, power plant or from the ambient air and “recycle” it into synthetic hydrocarbon fuels, alcohols or to chemicals instead of storing it in a geological formation.

With the re-use of captured CO₂, not only the reduction of present and upcoming emissive gas is ensured but also a beneficial carbon trajectory is obtained.

After the CO₂ is captured, for the purpose of attaining syngas, CO₂ is dissociated with assistance of a primary energy source, preferably renewable energy systems when they are not in demand or the electricity produced is in excess amounts. After attaining CO together with H₂ gas, there are several ways of putting recycled CO₂ into use. Direct production of synthetic fuels with Fischer-Tropsch method or alcohol synthesis can be made in order to close the cycle. When necessary, the synthetic fuel can chemically be converted into a storage medium (Amouroux et al., 2014) or directly injected to the existing grid (Graves, Ebbesen, Mogensen, & Lackner, 2011). Alternatively, the captured CO₂ can be used to produce chemicals, plastics or other materials.

Among all the steps taken towards the recycling of CO₂ process, dissociation of CO₂ to CO emerges as a critical phase since it requires a high initial energy when considering conventional conversion methods. Plasma-assisted dissociation under non-equilibrium conditions appears at this stage as a promising niche technology. While 5.5 eV is needed

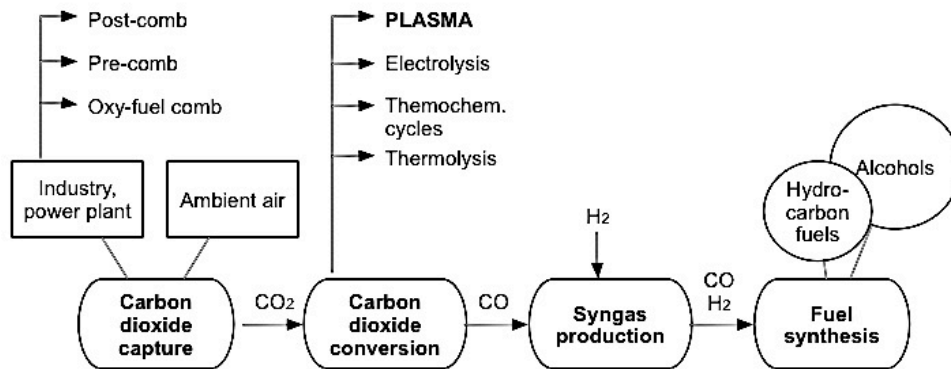


Figure 1. Overview of the proposed Carbon Capture and Recycling (CCR) Scheme.

to break the bonds in between the CO_2 molecule, non-thermal plasma system requires a lower initial energy in order to energize the electrons, initiate collisions and make the molecule vibrate. Under specific conditions, it is a viable technology to achieve an effective dissociation process even when the external discharge is turned off owing to vibrational excitation of the molecule. Additionally, plasma discharges are able to operate compatible with the renewable energy sources, which can lead the cycle to the most favorable trajectory by making it emission-free. However, along the dissociation processes there are limiting processes that should be addressed carefully. In this study, some of the important reactions and parameters are examined to better understand under which conditions the dissociation can be the most effective.

2. Introductory Concepts

2.1. Non-thermal Plasmas

In the plasma state heavy ions and light electrons coexist, sometimes together with neutrals, and the temperature of these species are not necessarily the same. In other words, plasmas are capable of displaying multiple temperatures. Temperature typically indicates the kinetic energy of particles in one state of matter (Fridman, 2008).

The non-equilibrium state is directly associated with non-thermal plasma systems where the temperature gradients differ from each other: electrons show the highest and gas the lowest temperature ($T_e > T_{\text{vib}} > T_g$) (Fridman, 2008). In cold plasmas, the gas temperature does not exceed too much the room temperature. The systems that are used for chemical processes are usually never kept in thermal equilibrium due to two main reasons: (1) confining and homogeneously heating a plasma medium is much more demanding than applying electromagnetic fields that can carry the charged species; (2) keeping the gas cold and accelerating only electrons to high velocities to initiate excitation yielding ionization of the molecules is quite often desirable. Some particular reactions are easy to

initiate when the electron energy distribution is suitable in non-thermal plasma systems (Nijdam, van Veldhuizen, Bruggeman, & Ebert, 2012).

2.2. Microwave Discharge (MD) Set-up

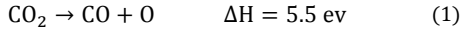
Microwave discharges (MD) are recently developed, powerful and energy-efficient set-up configurations that enable the generation of non-equilibrium plasmas with a high density. Along with the high electron density, they pave the way for a high electric field to be generated in a cold gas medium (Fridman, 2008).

In MD systems, a waveguide either perpendicular or parallel to the tube axis delivers microwaves in the suggested frequency operating in a continuum to provide excitation. The gas medium flows through this cylindrical system, which eventually consists of the plasma medium. MD systems are considered to be good candidates for applications involving hydrogen production and fuel conversion since they provide a powerful and energy-effective plasma system in a non-equilibrium condition entailing a highly productive but still less costly (e.g. electric energy) process (Fridman, 2008). When considering CO_2 plasma-assisted dissociation methods, MD is confirmed to offer the highest energy efficiency that can possibly be obtained (Kozák & Bogaerts, 2014; Silva, Britun, Godfroid, & Snyders, 2014). For this reason, environment conditions with regards to MD systems are used for the analysis of the plasma dissociation model proposed in this study.

2.3. Characteristics of CO_2 Molecule

Even though CO_2 is an abundant and easy-to-obtain molecule, it has a very low chemical energy level which makes it an insufficient matter for developing carbon based fuels (Tahir & Amin, 2013) without any prior processing. Hence, it is crucial to reduce it into CO before any further treatment. Similar to hydrogen, requiring a large separation energy (Chaffin et al., 2006), breaking the CO molecule from CO_2 is a demanding procedure due to its stable nature preserved at room temperature.

The enthalpy of CO₂ dissociation has a high rate under standard conditions (Fridman, 2008):



Since the main goal of conversion methods is to achieve maximized energy efficiency, a standard thermal dissociation process requiring severe conditions (e.g. fast quenching rate, temperatures around 2500-3000 K) does not emerge as the best option available. On the other hand, non-thermal plasmas, enhancing selectivity and chemical reactivity by exciting the species (Kozák & Bogaerts, 2014) offer an endothermic dissociation process of CO₂ molecule as presented in the following notation (Fridman, 2008) with the respected dissociation energy:



Thus, as in the case of non-thermal plasmas, an optimal system can be established in terms of a lower energy input, which can set off molecule interactions entailing a non-equilibrium vibrational state. Cold plasma can enhance the chain of reactions by means of reduced gas temperatures that consequently offer low rates of reverse reactions taking place. Moreover, reduced gas temperatures from discharge to afterglow phases can entail a higher V-V effect (Fridman, 2008).

3. Analysis of the Performed Model

3.1. Vibrational Modes of CO₂

CO₂ is a triatomic molecule, however, owing to its structure presenting linear properties, it behaves like a simple diatomic molecule representing three modes of vibration in its ground electronic state independent from each other: symmetric valence vibration, double degenerated symmetric vibration and asymmetric vibration with corresponding quantum numbers: v_1, v_2, v_3 (Silva et al., 2014).

In order to aggrandize the initial vibration energy and overcome the dissociation barrier, it is crucial to conserve the vibration state of the molecule (Goede et al., 2014). Among the three normal vibrational modes of CO₂ molecule, the asymmetric vibration mode carries an explicit significance since (1) the energy losses associated with vibrational-translational (V-T) are far lower than those in the symmetric vibration and bending modes; (2) intra-mode (V-V) energy interchange happens very fast favoring the aggregation of highly energized states of asymmetric mode; (3) this mode is predominantly excited by electrons having temperatures between 1-3 eV (Kozák & Bogaerts, 2014; Silva et al., 2014). Based upon these arguments, the vibration energy levels of asymmetric mode [CO₂(00 v_3)] are taken into consideration solely along the equations in the excitation and de-excitation of the corresponding

study, whereas symmetric (v_1) and bending modes (v_2) are neglected to narrow down the scope and simplify the equations.

3.2. The Reactions of the Vibrational Levels

The reaction kinetics in this thesis follows the extended model presented by the recent work of Kozák et al. (Kozák & Bogaerts, 2014) in scope of two main types of reactions: (1) electron impact excitation (e-V); and (2) vibrational energy exchange reactions (V-T) and (V-V). Unlike the abovementioned literature, the impact of chemical reactions and first four levels of symmetric mode vibration are disregarded in this study for simplifying the equations related to complex chemistry of the CO₂ molecule. The main focus is given to the reactions with the most impact on the dissociation process.

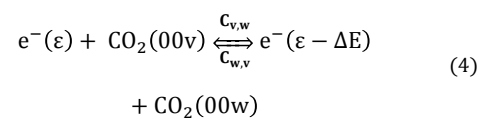
Vibration levels of CO₂ molecule involved in the model are presented from ground to dissociation (21st) level and their energies (in eV) are calculated according to the following notation provided in the source (Fridman, 2008) by considering only the asymmetric levels. In this notation anharmonicity coefficients are taken as $x_{33} = -1.6 \times 10^{-3}$ eV, $x_{13} = -2.4 \times 10^{-3}$ eV, $x_{23} = -1.6 \times 10^{-3}$ eV respectively. The further details of the notation can be found in Fridman (Fridman, 2008).

$$E_v(v_3) = \hbar w_3 \left(v_3 + \frac{1}{2} \right) + x_{33} \left(v_3 + \frac{1}{2} \right)^2 + x_{13} \left(v_1 + \frac{1}{2} \right) \left(v_3 + \frac{1}{2} \right) + x_{23} (v_2 + 1) \left(v_3 + \frac{1}{2} \right) \quad (3)$$

Three modes of vibrational exchange, which occur simultaneously, are calculated individually in this section and are evaluated in terms of time progression of plasma species' densities in a specific plasma volume. Initially (1) electron impact excitation (e-V) and (2) vibrational energy exchange reactions, which are divided in two: vibration to translation energy exchanges (V-T) and vibration to vibration energy exchanges (V-V) are assessed.

3.2.1. Electron Impact Excitation (e-V)

This energy exchange process refers to the transferal of input energy from electrons to CO₂ molecules. The elementary descriptive equation of electron to vibration energy exchanges can be expressed as in the following dual notation:



The molecule's asymmetric level alternates from v to w . $C_{v,w}$ and $C_{w,v}$ define the rate coefficients for

states respectively, change from initial state ε_i to $(\varepsilon_i - \Delta E)$ demonstrates the energy decrease of the electron that excites the molecule. The electron energy distribution function, EEDF, which is highly dependent on the gas composition and electric field in cold plasma discharges, occasionally shows a very different distribution than in equilibrium conditions (Fridman, 2008). However, for the purposes of this work and in order to keep the problem simple, a Maxwellian EEDF is considered. In terms of electron energy, the EEDF can be modified as (M. Capitelli, C.M. Ferreira, B.F. Gordiets, 2000) where the kinetic energy is $u=1/2m_e v^2$. The constant C is later obtained from normalization condition (M. Capitelli, C.M. Ferreira, B.F. Gordiets, 2000). And the corresponding cross section for the excitation of the first level is collected from (Janeco, Pinhão, & Guerra, 2015), which follows a similar trend than that of (Itikawa, 2002):

$$f(u) = C * \exp\left[-\frac{u}{kT_e}\right] \quad (5)$$

The excitation rate coefficient can be calculated from an average over the EEDF, where $u_{0,1}$ is the threshold energy approximately equal to 0.294 eV:

$$C_{0,1} = \langle \sigma_{0,1}(u)v \rangle = \sqrt{\frac{2}{m_e}} \int_{u_{0,1}}^{\infty} \sigma_{0,1}(u)\sqrt{u} f(u) du \quad (6)$$

Cross sectional area defines the probability of a collision occurring under respected conditions. In consequence of lack of data regarding the excitation of higher asymmetric mode vibration levels', the excitation cross sections ($\sigma_{i,j}$) from an initial excitation level $CO_2 v_i$ to final level $CO_2 v_j$ are obtained from the semi-empirical approximation of Fridman (Fridman, 2008) by taking the known cross section $\sigma_{0,1}$ (from ground state to level 1) as the base. For the numerical calculation of this approach, the equation is modified as predicated on the references (Fridman, 2008; Kozák & Bogaerts, 2014):

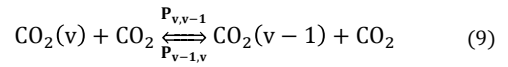
$$\sigma_{i,j}(u) = \exp\left(-\frac{\alpha(j-i)}{1+\beta n}\right) * \sigma_{0,1}\left(u + \frac{E_{0,1}}{E_1-E_0} - \frac{E_{i,j}}{E_j-E_i}\right) \quad (7)$$

The asymmetric energy levels are found from equation 3. α is taken as 0.5 and β as 0 as it is suggested in Fridman (Fridman, 2008), in good agreement with the reference paper (Kozák & Bogaerts, 2014). Therewith, the magnitudes of the cross sections are scaled with respect to parameters α and β . Finally, for the super elastic collisions (reverse reaction rates, $C_{w,v}$, where $w < v$) resulting from the de-excitation of molecules, the cross sections are obtained with regards to detailed balance equation:

$$C_{w,v} = C_{v,w} \frac{[CO_2(v)]}{[CO_2(w)]} = C_{v,w} * \exp\left[-\frac{E_v - E_w}{kT_e}\right] \quad (8)$$

3.2.2. Vibration to Translation Energy Exchanges (V-T)

The energy transfer process from vibration to translational degrees of freedom is called vibrational relaxation (V-T) (Fridman, 2008). In V-T energy exchange reactions, the vibrational quanta, hence the vibrational energy, is lost to kinetic energy and thus this exchange mechanism is referred as V-T "relaxation" and is an undesirable step for the overall dissociation process. Therefore, when considering the complete V-T process, vibrational energy is mainly lost:



To calculate the rate constants of V-T energy exchange in collisions occurring amongst molecules, first order Schwartz-Slowsky-Herzfeld (SSH) theory, which provides a comparatively simple definition for the state-specific relaxation degree is used for the kinetic model in accordance with the literature (Kozák & Bogaerts, 2014) where $P_{v,v-1}$ represents the rate constant of V-T relaxation from level v to $(v-1)$, and $P_{1,0}$ is the rate constant for the $v=1$ to $v=0$ transition:

$$P_{v,v-1} = \frac{P_{1,0} * Z_v * F(\gamma_v)}{F(\gamma_1)} \quad (10)$$

After the basic rate constants ($P_{1,0}$ for V2a, V2b, V2c) are collected from the literature (Kozák & Bogaerts, 2014) as they are presented in Table 1 subsequent rate constants are derived from equation 10. The relevant parameters; Z_v (the scaling factor) and γ_v (measure of adiabaticity) are calculated from the relations given in the reference paper (Kozák & Bogaerts, 2014). Non-dimensional anharmonicity energy level, x_e , is extracted from the literatures (Kozák & Bogaerts, 2014, 2015) considering relevant vibrational energy transfer reactions of CO_2 (Table 1). Finally the adiabaticity factor, function $F(\gamma)$, is evaluated from the following formula, which is approximated with respect to Keck and Carrier (1965) empirical fit for $0 \leq \gamma \leq 20$ and Schwartz and Herzfeld (1954) expression for $\gamma > 20$ (Loureiro & Ferreira, 1986):

$$F(\gamma) = \gamma^2 \int_0^x e^{-x} \operatorname{cosech}^2\left(\frac{\gamma}{\sqrt{x}}\right) dx \quad (11)$$

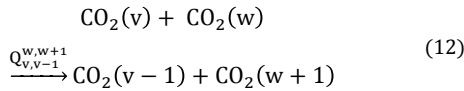
The reverse reaction rates ($P_{v-1,v}$) are obtained from the detailed balance equation similar to the one of e-V exchanges by taking T_g into account instead of T_e (Loureiro & Ferreira, 1986).

Table 1. Vibrational energy transfer reactions of CO₂ (Kozák & Bogaerts, 2014, 2015).

No.	Ref.	Reaction	Initial rate constant [cm ³ s ⁻¹]	x _e (10 ⁻³)
V2a	(Kozák & Bogaerts, 2014)	CO ₂ v _i + M ⇌ CO ₂ v _{i-1(a)} + M	0.43 * exp(-407 * T _g ^{-1/3} + 824 * T _g ^{-2/3})	3.7
V2b		CO ₂ v _i + M ⇌ CO ₂ v _{i-1(b)} + M	0.86 * exp(-404 * T _g ^{-1/3} + 1096 * T _g ^{-2/3})	1.0
V2c		CO ₂ v _i + M ⇌ CO ₂ v _{i-1(c)} + M	1.43 * 10 ⁻⁵ * exp(-252 * T _g ^{-1/3} + 685 * T _g ^{-2/3})	-15.6
V6	(Kozák & Bogaerts, 2015)	CO ₂ v _i + CO ₂ v _j ⇌ CO ₂ v _{i-1} + CO ₂ v _{j+1}	1.8 * 10 ⁻¹¹ * exp(-24.7 * T _g ^{-1/3} - 65.7 * T _g ^{-2/3})	5.25

3.2.2. Vibration to Vibration Energy Exchanges (V-V)

The third and final type of exchange collisions that take place between excited CO₂ molecules is denoted as vibration to vibration (V-V), involving two indicators: one molecule in which the vibrational state is reduced from v to (v-1), and the other in which the vibrational state is raised from w to (w+1) (Kozák & Bogaerts, 2014) as determined in the following notation:



In vibrational degrees of freedom exchanges, the transition may correspond to a V-V exchange among two molecules of the same vibrational mode, such as between asymmetric levels (intra-mode transition), and to a V-V' (inter mode transition), denoting an exchange among two different modes of vibration (e.g. among bending and asymmetric levels). Similar to previous exchange models, asymmetric levels (intra mode) are involved in the respected calculations. The basis of this simplification is predicated on the reaction speed, where V-V exchanges within the asymmetric mode show faster kinetics in several orders of magnitude than the symmetric mode, escalating the population of highly energized vibrational states in the asymmetric mode (Fridman, 2008).

Similar to V-T reactions, the rate coefficients for V-V are also obtained from SSH theory adapted by Bray (1967) for this specific case (Kozák & Bogaerts, 2014; Loureiro & Ferreira, 1986):

$$Q_{v,v-1}^{w,w+1} = Q_{1,0}^{0,1} * Z_v * Z_w * \left(\frac{F(\gamma_{vw})}{F(\gamma_{11})} \right) \quad (13)$$

To find the required parameters, same formulas as in V-T exchanges are used for the parameters Z_v, γ_v, F(γ) pursuant to modifications based on two indicators instead of one. The initial rate coefficient value, as well as x_e are collected from Table 1 for V6 factor. As the final step of the reaction kinetics, the reverse reactions are obtained from detailed balance equation (Loureiro & Ferreira, 1986).

4. Results and Discussion

4.1. Evaluation of the Vibration Kinetics

Before the plasma is switched on, the CO₂ molecules are distributed according to an equilibrium distribution at the environment gas temperature ~300 K. When a discharge is applied, if there are only e-V energy exchanges, the molecules eventually reach an equilibrium with the electrons and their distribution is characterized by the electron temperature, T_e. When the discharge is switched off, electrons vanish and the molecules relax and once more reach an equilibrium state with T_g. Under the influence of e-V exchanges only, no afterglow effect can be observed. This is mainly due to the disappearance of electrons (n_e=0) when the discharge is switched off. Since there are no electrons in the afterglow phase, no process by electron impact takes place. However, the expected result at the afterglow phase is the decrease of densities and equilibrium of the population curve with the ambient gas. This relaxation mechanism is studied within the framework of V-T and V-V exchange processes.

When the e-V and V-T processes are both activated, the Boltzmann distribution loses its validity and the molecules reach a thermodynamically non-equilibrium but steady state (i.e. stationary with time) vibrational distribution. At the discharge phase (1), a decrease of the curve caused by the translational energy losses is observed. Furthermore, in the afterglow phase (2), CO₂ molecules unfavorably lose energy based upon the V-T relaxation in the millisecond time scale.

To observe the effect of V-V in absence of the destructive V-T at the discharge phase, population and density distribution of the molecules when T_g=300 K are plotted. According to the population regime of CO₂ molecules, a hyperbolic plateau distribution (i.e. Treanor) is observed. As a consequence, inversion of population among the levels of vibration can be seen after a certain vibration level (Treanor, C. E., Rich, J.W., Rehm, 1968). Even though when the discharge is removed the same final state as with V-T relaxation only takes place at t=∞, the intermediate excitation stages

are eligible to bring out a plateau regime that favors the decomposition process. The preliminary results show the eligibility of an effective decomposition when the discharge is turned off as long as the negative impact of V-T relaxation is somewhat precluded or the V-V is promoted over the complete process. This may be achieved by improving the gas temperature differences between the discharge and afterglow phases and/or tuning the process to a specific afterglow time, as discussed in the following section.

4.2. Altering the Process Parameters

4.2.1. Reference Case Involving All Three Transfers

A reference case is created in order to compare the results when the process parameters are altered. Afterglow gas temperature is assumed to be less than the initial temperature. This is mainly based on the targeted afterglow effect, where the dissociation can still be promoted when the power is shut off. Hence, in the performed reference model, T_g is taken as 500 K at the discharge phase and 300 K at the afterglow phase assuming a cooling effect. The gas pressure is kept at 2660 Pascal and the electron temperature is assumed to be 0.5 eV. Electron density, n_e , is assigned to $5 \times 10^{10} \text{ cm}^{-3}$. This relatively idealized system, as can be observed in Figure 2, is to prove that an effective dissociation can be achieved when the V-V transfer is promoted with providing a difference in the gas temperature of discharge and afterglow phases.

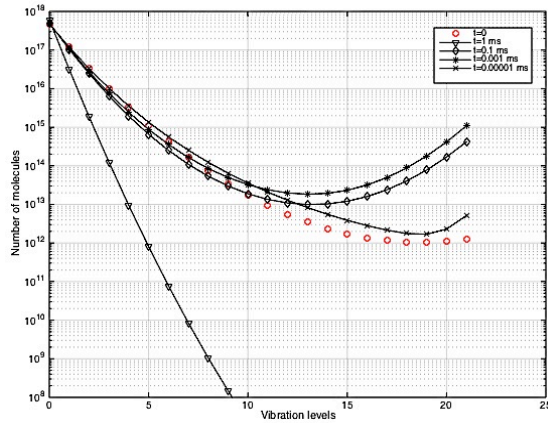


Figure 2. Population distribution curve of the reference case in the afterglow phase in different time scales.

4.2.2. Results After Modifying the Pressure and the Electron Density

To observe how the population distribution varies with respect to the change in gas pressure, P_g , 266 Pa, 2000 Pa, 3500 Pa, 8000 Pa and 101325 Pa (=1 atm) is compared to the reference value, 2660 Pa. Eventually, increase and decrease of pressure is found to impact the process negatively. The optimum pressure is proved to be around 2660 Pa, where the population distribution reaches its ideal state in the afterglow phase.

To observe the electron density impact on the dissociation process, some different values for electron density are assigned in the numerical model, whereas the other parameters are set to the reference values. A lower value ($1 \times 10^9 \text{ cm}^{-3}$) and a higher value ($1 \times 10^{12} \text{ cm}^{-3}$) is given to compare them with the reference case $n_e = 5 \times 10^{10} \text{ cm}^{-3}$. When compared to the reference curve, the decrease of the electron density found to show a negative influence on the overall process. A Treanor distribution is no longer observed when the electron density is lowered down to $1 \times 10^9 \text{ cm}^{-3}$ from the reference value. However, a better result is obtained when it is increased up to $1 \times 10^{12} \text{ cm}^{-3}$. When there are more electrons, more collisions take place, transferring more energy from electrons to vibration. Nevertheless, an increase of the electron density can only be provided by increasing the discharge current. As a result, the supplied power will increase. From an economical point of view, this may be practically unfeasible.

4.2.3. Temperature Dependence of the Process

4.2.3.1. Altering the Gas Temperature

Temperature of the gas is an important factor when considering gaseous discharges. It describes the energy distribution of the gaseous particles, also known as “heavy” particles (Chen et al., 2015). When assessing the influence of three different energy exchanges, it is shown that the temperature difference between the discharge and afterglow phases influence the dissociation positively if the temperature is lowered in the afterglow phase.

It is observed that lowering the temperature of the afterglow phase increases the dissociation rate. Hence, among the values ($T_{g(\text{afterglow})} = 300 \text{ K}, 290 \text{ K}, 280 \text{ K}$) considered, 280 K is observed as the most effective afterglow temperature obtained in our model. Subsequently, the gas temperature at the discharge phase is increased from 500 K to 525 K, 550 K and to 600 K respectively. The temperature increase in this case contributes to the vibrational population distribution negatively, decreasing the number of molecules in higher levels. As the final practice regarding gas temperatures, the temperature at the discharge phase is lowered from 500 K to 400 K and to 320 K while the afterglow phase gas temperature is kept in 280 K, which was observed as the most favorable value. As can be seen from Figure 3, the decreasing temperature rate did not present a parallel decrease. Instead, the optimal population distribution curve is observed at 400 K instead of 320 K.

In Figure 3, competition of two effects, V-T and V-T, can be observed. As mentioned before, if there is a big difference of gas temperature between the discharge and afterglow phases, the V-V pumping effect can be promoted. However, the rise in the gas temperature increases V-T deactivation. So, the gap

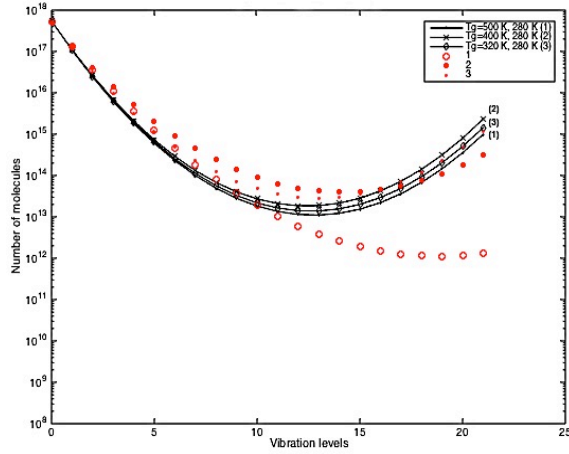


Figure 3. Comparison of population distribution curves at the afterglow phase where $T_{g(\text{discharge})}=500\text{ K}$, 400 K , 320 K and $T_{g(\text{afterglow})}=280\text{ K}$ ($t_{\text{afterglow}}=0.1\text{ ms}$).

between the discharge and afterglow gas temperatures should be kept at a maximum rate without increasing too much the gas temperature at the discharge phase. In this case, the most favorable discharge phase gas temperatures are observed around 400 K .

4.2.3.2. Altering the Electron Temperature

Lowering the electron temperature from 0.5 eV to 0.3 eV did not have a constructive influence on the process. The electron temperature is increased from 0.5 eV to 2 eV and to upper values. The electron temperature increase from 0.5 eV to 2 eV showed a constructive effect. Further increase kept contributing to the curve positively. However, the contribution of increased electron temperature is started to show smaller enhancement above values 2 eV .

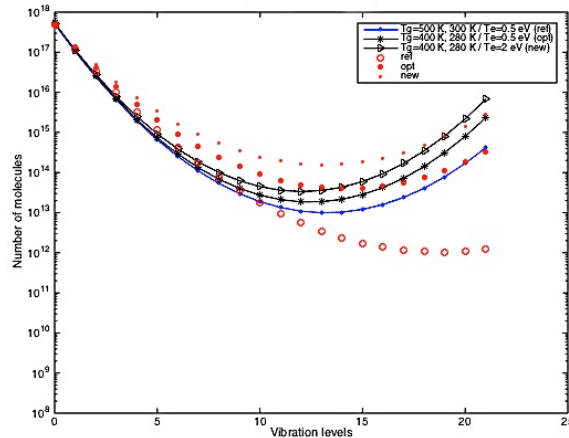


Figure 4. Comparison of population distribution curves of the reference, optimum and the new cases at the afterglow phase ($t_{\text{afterglow}}=0.1\text{ ms}$).

Two better scenarios are obtained when compared to the reference case (Figure 4). The most effective curve under previously assigned conditions is found to be the one with optimum gas and electron

temperatures ($T_g=400\text{ K}$, 280 K and $T_e=2\text{ eV}$). Even though the increase of electron temperature entails more electron creation, it requires higher start-up energy. Keeping the electron temperature at 0.5 eV rather than 2 eV is a better result from the economical point of view since it indicates a lower initial energy is requirement. Therefore, the overall system can operate economically more feasibly.

5. Conclusion

As a result of the energy exchange reactions, it is shown that an effective dissociation process under specific conditions is possible to achieve. A Treanor distribution is observed from the preliminary results when the effects of e-V and V-V are involved, whereas V-T is excluded from the model at gas temperatures around the room temperature at both the discharge and afterglow phases. However, when the V-T was included, the population distribution showed an abrupt decrease unfavorably affecting the dissociation process. To assess under which conditions the negative V-T effect could be decreased or the positively contributing V-V effect can be promoted, different cases with varying process parameters are created and compared to the reference case.

It is well understood that the gas temperature has a crucial impact on the overall process. The optimal results are obtained when there is a temperature difference of the gas between the discharge and afterglow phases. However, when the temperature was increased too much, negative V-T effect stepped in. Competition of two effects, V-T's deactivation and V-V's pumping, is presented with the comparison of different curves plotted with respect to variable discharge and afterglow gas temperatures.

The conclusions we can take in this study are more qualitative than quantitative. Nevertheless, it was possible to obtain an optimal point with quantitative results. Within the scope of our hypothesis, the optimal gas temperature is found to be around 400 K for the discharge phase and 280 K for the afterglow phase (at $T_e=0.5\text{ eV}$), assuming a strong cooling effect.

In this study, preliminary qualitative results are obtained in order to observe the destructive effect of V-T and promoting effect of V-V. As it is obvious from the results, enhancement of the V-V process positively contributes to the overall dissociation process. In order to achieve quantitative results, other vibrational modes of CO_2 molecule (such as symmetric and bending stretching) as well as the chemical reactions can further be involved in the model in future studies.

References

- Amouroux, J., Siffert, P., Pierre Massué, J., Cavadias, S., Trujillo, B., Hashimoto, K., ... Wang, X. (2014). Carbon dioxide: A new material for energy storage. *Progress in Natural Science: Materials International*. doi:10.1016/j.pnsc.2014.06.006
- Andres, R. J., Boden, T. a., Bréon, F. M., Ciais, P., Davis, S., Erickson, D., ... Treanton, K. (2012). A synthesis of carbon dioxide emissions from fossil-fuel combustion. *Biogeosciences*, 9, 1845–1871. doi:10.5194/bg-9-1845-2012
- Boretti, A. (2013). Renewable hydrogen to recycle CO2 to methanol. *International Journal of Hydrogen Energy*, 38(4), 1806–1812. doi:10.1016/j.ijhydene.2012.11.097
- Chaffin, J. H., Bobbio, S. M., Inyang, H. I., & Kaanagbara, L. (2006). Hydrogen Production by Plasma Electrolysis. *Journal of Energy Engineering*, 132, 104–108. doi:10.1061/(ASCE)0733-9402(2006)132:3(104)
- Chen, G., Silva, T., Georgieva, V., Godfroid, T., Britun, N., Snyders, R., & Delplancke-Ogletree, M. P. (2015). Simultaneous dissociation of CO2 and H2O to syngas in a surface-wave microwave discharge. *International Journal of Hydrogen Energy*, 40(9), 3789–3796. doi:10.1016/j.ijhydene.2015.01.084
- Fridman, A. (2008). *Plasma Chemistry*. Cambridge University Press.
- Goede, A. P. H., Bongers, W. a, Graswinckel, M. G., Sanden, R. M. C. . Van De, Martina, L., Jochen, K., ... Mathias, W. (2014). Production of Solar Fuels by CO2 Plasmolysis. In *3rd European Energy conference Budapest* (Vol. 01005, pp. 1–5). Retrieved from <http://dx.doi.org/10.1051/epjconf/20137901005>
- Goeppert, A., Czaun, M., Jones, J.-P., Surya Prakash, G. K., & Olah, G. a. (2014). Recycling of carbon dioxide to methanol and derived products - closing the loop. *Chemical Society Reviews*, 43(23), 7995–8048. doi:10.1039/c4cs00122b
- Graves, C., Ebbesen, S. D., Mogensen, M., & Lackner, K. S. (2011). Sustainable hydrocarbon fuels by recycling CO2 and H2O with renewable or nuclear energy. *Renewable and Sustainable Energy Reviews*, 15, 1–23. doi:10.1016/j.rser.2010.07.014
- Itikawa, Y. (2002). Cross sections for electron collisions with carbon dioxide. *Journal of Physical and Chemical Reference Data*, 31(3), 749–767. doi:10.1063/1.1481879
- Janeco, A., Pinhão, N. R., & Guerra, V. (2015). Electron kinetics in He / CH4 / CO2 mixtures used for Methane conversion. *The Journal of Physical Chemistry*, 119(1), 109–120. doi:10.1021/jp509843e
- Kozák, T., & Bogaerts, A. (2014). Splitting of CO2 by vibrational excitation in non-equilibrium plasmas: a reaction kinetics model. *Plasma Sources Science and Technology*, 23, 045004. doi:10.1088/0963-0252/23/4/045004
- Kozák, T., & Bogaerts, A. (2015). Evaluation of the energy efficiency of CO2 conversion in microwave discharges using a reaction kinetics model. *Plasma Sources Science and Technology*, 24, 015024. doi:10.1088/0963-0252/24/1/015024
- Loureiro, J., & Ferreira, C. M. (1986). Coupled electron energy and vibrational distribution functions in stationary N2 discharges. *Journal of Physics D: Applied Physics*, 19, 17. Retrieved from <http://stacks.iop.org/0022-3727/19/i=1/a=007>
- M. Capitelli, C.M. Ferreira, B.F. Gordiets, A. I. O. (2000). *Plasma Kinetics in Atmospheric Gases* (1st ed.). Springer-Verlag Berlin Heidelberg GmbH. doi:10.1007/978-3-662-04158-1
- Nijdam, S., van Veldhuizen, E., Bruggeman, P., & Ebert, U. (2012). Plasma Chemistry and Catalysis in Gases and Liquids. In *An Introduction to Nonequilibrium Plasmas at Atmospheric Pressure* (1st ed., pp. 1–44). Wiley. doi:10.1002/9783527649525.ch1
- Olah, G. A., Prakash, G. K. S., & Goepfert, A. (2011). Anthropogenic Chemical Carbon Cycle for a Sustainable Future. *Journal of The American Chemical Society*, 133, 12881–12898. doi:dx.doi.org/10.1021(ja202642y)
- Silva, T., Britun, N., Godfroid, T., & Snyders, R. (2014). Optical characterization of a microwave pulsed discharge used for dissociation of CO2. *Plasma Sources Science and Technology*, 23(2), 025009. doi:10.1088/0963-0252/23/2/025009
- Tahir, M., & Amin, N. S. (2013). Recycling of carbon dioxide to renewable fuels by photocatalysis: Prospects and challenges. *Renewable and Sustainable Energy Reviews*, 25, 560–579. doi:10.1016/j.rser.2013.05.027
- Treanor, C. E., Rich, J.W., Rehm, R. G. (1968). Vibrational Relaxation of Anharmonic Oscillators with Exchange-Dominated Collisions. *The Journal of Chemical Physics*, 48(4), 1798–1807. doi:10.1063/1.1668914