CO₂ conversion in a microwave plasma reactor in the presence of N₂: modelling and experimental validation

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Abstract: We present a chemical kinetics model for a CO₂/N₂ microwave plasma, with special emphasis on the vibrational levels of both CO₂ and N₂. The model results, like CO₂ and N₂ conversion, and the energy efficiency, are in reasonable agreement with experiments, for different power densities and for N₂ fractions in the CO₂/N₂ gas mixture ranging from 0 till 90%. The observed trends are explained based on the destruction processes of CO₂, and on the vibrational distribution functions of CO₂.

Keywords: microwave, CO₂ conversion, vibrational, N₂ conversion, 0D model

1. Introduction
Plasma-based conversion of CO₂ into value-added chemicals or fuels, by means of different types of plasmas [1-4], is gaining increasing interest. A microwave (MW) plasma is of particular interest [3], because of the high energy efficiencies reported under some conditions [1, 4]. These high efficiencies are due to the dissociation of highly vibrationally excited CO₂ [1, 4].

Most experiments in literature are carried out in pure CO₂ [2, 3], or in combination with CH₄ (i.e., dry reforming) [5] or an inert gas [6]. However, real gas emissions from combustion or the chemical industry are not only composed of pure CO₂, but also of other molecular gases, such as N₂. Therefore, it is of great importance to investigate the effect of N₂ on the CO₂ conversion and on the energy efficiency. A few experiments have been performed for CO₂/N₂ mixtures [7, 8], but not yet for a microwave plasma.

2. Description of the Model
We used a zero-dimensional (0D) chemical kinetics model, called ZDPlaskin [9], which calculates the time-evolution of the species densities by balance equations, based on the various production and loss terms by chemical reactions. The rate coefficients of these reactions are adopted from literature for the heavy particle reactions, while they are calculated with a Boltzmann solver, BOLSIG+ [10], for the electron impact reactions. Scaling theories, i.e., the Forced Harmonic Oscillator (FHO) theory [11], and the Schwartz, Slawsky and Herzfeld (SSH-) theory [12], are used to calculate the rate coefficients of vibration induced reactions with highly vibrationally excited particles from the rate coefficients of these reactions with the particles residing in the lowest vibrational levels.

3. Description of the Experiments
The experiments are done in a microwave discharge generated with a 915 MHz microwave generator in a double-walled quartz tube with 14 mm inner diameter and about 20 cm length (see Fig. 1) at an initial gas temperature of 300 K, a pressure of 2660 Pa, gas fractions ranging from 0 till 90%, a gas flow rate of 5 slm (standard litres per minute) and at power densities of 30, 50 and 80 W/cm³.

4. Results and Discussion
Our model is based on the reaction kinetics model developed earlier for the dissociation of pure CO₂ in a MW plasma and a dielectric barrier discharge [13, 14], including state-to-state reactions of vibrational levels of CO₂ and CO, and it is extended to a CO₂/N₂ mixture. The species included in our model are various neutral molecules in the ground state, as well as electronic and vibrationally excited levels of CO₂, CO, N₂ and O₂, various radicals, positive and negative ions, and the electrons. Besides the input gases (CO₂ and N₂), also various formed products are included, such as CO, O₂, O₃, several NOx compounds, as well as some other CO₂-derived compounds, N-C and N-C-O compounds. Because the asymmetric mode levels are most important for the splitting of CO₂ [1, 4], all these levels up to the dissociation limit are included in the model (i.e., 21 levels), whereas only a few symmetric mode levels are incorporated, following the example of the model developed by Kozák et al. [13]. In the case of N₂, 14 levels are used. More details about this model can be found in [15].

Figure 1: Schematic diagram of the microwave plasma reactor setup.
increasing the N\textsubscript{2} fraction, the CO\textsubscript{2} conversion rises. The effective CO\textsubscript{2} conversion, on the other hand, which is calculated by multiplying the CO\textsubscript{2} conversion with the initial CO\textsubscript{2} fraction, drops with increasing N\textsubscript{2} fraction. This is of course due to the lower CO\textsubscript{2} content in the gas mixture. The same is true for the energy efficiency, which is dependent of the effective CO\textsubscript{2} conversion. Because the energy efficiency of CO\textsubscript{2} conversion can be linked to the concentration of (highly) vibrationally excited CO\textsubscript{2} \cite{1, 4}, it is likely that N\textsubscript{2} vibrationally interacts with CO\textsubscript{2}. To explain the effect of N\textsubscript{2} addition on the CO\textsubscript{2} conversion and energy efficiency, we have studied the vibrational kinetics of CO\textsubscript{2} and N\textsubscript{2}, together with their destruction and formation mechanisms.

The contributions of the most important conversion mechanisms of CO\textsubscript{2} at 80 W/cm\textsuperscript{3} are given in Fig. 3. With increasing N\textsubscript{2} fraction the total contribution of all reactions with vibrationally excited CO\textsubscript{2} increases. These contributions are linked to the vibrational distribution functions (VDFs) of the asymmetric mode levels of CO\textsubscript{2} which are given in Fig. 4 for the power density of 80 W/cm\textsuperscript{3}.

![Fig. 1. Schematic representation of the microwave generator and the gas chromatograph.](image1)

![Fig. 2. CO\textsubscript{2} conversion (a) and energy efficiency (b) as a function of N\textsubscript{2} fraction.](image2)

![Fig. 3. Relative contributions of the most important conversion processes of CO\textsubscript{2}, as a function of N\textsubscript{2} fraction in the gas mixture at 80 W/cm\textsuperscript{3}.](image3)

![Fig. 4. Vibrational distribution functions (VDFs) of the asymmetric mode vibrational levels of CO\textsubscript{2}, obtained at the end of the simulations, at 80 W/cm\textsuperscript{3}, and N\textsubscript{2} fractions of 10%, 50% and 90%.](image4)
The VDFs show that with rising N₂ concentration the fraction of (highly) vibrationally excited CO₂ increases, which explains the findings in Fig. 3, i.e., the increase of the total contribution of conversion mechanisms with vibrationally excited CO₂ with rising N₂ fraction. N₂ helps vibrationally exciting CO₂. More specifically, N₂ transfers its vibrational energy towards the lower asymmetric mode levels of CO₂ through VV-relaxation [1, 4, 8]. From these lower levels the higher levels are then populated using VV-relaxation with CO₂/CO.

5. Conclusions
A 0D chemical kinetics model is developed for a CO₂/N₂ microwave plasma, with special emphasis on the vibrational levels of both CO₂ and N₂. The model is used to calculate the CO₂ and N₂ conversion, as well as the energy efficiency for CO₂ conversion, at a gas pressure of 2660 Pa and a gas inlet temperature of 300 K, for three different values of power density in the range of 30 - 80 W/cm³, and for N₂ fractions in the gas mixture ranging from 0 till 90% N₂.

The absolute CO₂ conversion rises with increasing N₂ fraction. This indicates that N₂ has a beneficial effect on the CO₂ conversion. The effective CO₂ conversion, on the other hand, drops upon rising N₂ fraction, as there is less CO₂ present in the gas mixture. The drop in energy efficiency is simply a result of the lower effective CO₂ conversion upon rising N₂ fraction.

The calculated VDFs of CO₂ illustrate that the vibrational levels of CO₂ are most important at high N₂ fractions where N₂ helps populating the lower asymmetric levels through VV-relaxation. This explains the rise of the total contribution of all reactions with vibrationally excited CO₂ with increasing N₂ fraction.

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7. References