1D modelling of the CO_2 conversion in microwave discharges

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Carbon monoxide CO required (together with H_2) for production of synthetic fuels can be obtained by splitting of CO_2 from the exhaust gases. It was reported in the past that a very high energy efficiency η of the $CO_2 \rightarrow$CO conversion - up to η=80 % and more - can be achieved in 2.5 GHz microwave (MW) gas discharges at reduced pressures ($\sim$100 Torr) [1]. Those record high values have not yet been reproduced in nowdays experiments [2], although in some of them η up to 60 % was reached [3]. For better theoretical understanding and optimization of experiments a detailed chemical kinetics model of the CO_2 plasma has been developed recently [4]. On the basis of this model 0D time-dependent calculations with prescribed electron density were made [5]. They give the maximum η of only 32 %, in a striking difference with both experimental and theoretical results reviewed in [1]. The reaction kinetics of [4] was later revised in [6]. In the present work the set of reactions published in [6, 7] is used in a simple 1D model of a chemical reactor where the electron-density is calculated self-consistently. The ability of this model to reproduce the results presented in [1] is examined.

Technically the reaction data set [6, 7] is implemented in a self-written program by translating the published input file [7] into Fortran code. To estimate the variation of the results with respect to different kinetics models used, a comparison is made with X and η dependencies of SEI calculated in [4], see Figure 1. Here X is the conversion rate, η is the energy efficiency, same definitions as in [4]; SEI is the Specific Energy Input per CO_2 molecule. The 0D time-dependent calculations are made with fixed temperature of heavy particles (300 K). The temperature of electrons is found from the energy balance, as described in [4, 6]. The pressure 20 Torr, and residence time in the discharge zone 9.13 ms correspond to "MW discharge" case in [4]. The input power density in the discharge is varied to obtain a variation of SEI.

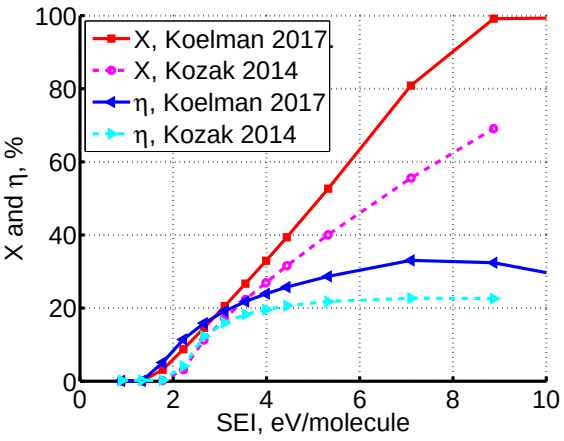

Figure 1: Comparing the results obtained with reaction kinetics [6, 7] ("Koelman 2017") and [4] ("Kozak 2014")

Qualitatively the dependencies obtained in two independent calculations are similar: nearly linear growth of X, saturation of η at high SEI. However, quantitative difference reaches almost a factor of 2.

The model of the 1D plasma flow in a reactor channel is based on two assumptions which greatly simplify the equations. First, it is assumed that all species i have the same velocity $v_i = v$ along the channel axis x. Second, only flows with low mach number $M < 1$ are considered. For low degree of ionization, when the electron pressure p_e is much smaller than p_h, this second assumption leads to the momentum balance $p_h = T_h \sum_i n_i = const$. Here p_h is the pressure of "heavies" - molecules, atoms and ions; n_i is the density of species i, T_h is the translational-rotational (TR) temperature of heavies. TR degrees of freedom are assumed to be in equilibrium, vibrationally and electronically excited states are described as separate species. The resulting set of the particle and energy balance equations reads as follows:

$$\frac{d\Gamma_i}{dx} = S_i, \quad n_i = \frac{\Gamma_i}{\sum_i \Gamma_i}\frac{p_h}{T_h}, \quad n_e = \sum_i Z_i n_i$$

$$\frac{dT_e}{dx} = \frac{P_{in} - Q^e_{elastic} - Q^e_{inelastic} - 2.5T_e \sum_i Z_i S_i}{2.5\sum_i Z_i \Gamma_i}, \quad \frac{dT_h}{dx} = \frac{Q^e_{elastic} + Q^{e\to h}_{inelastic} - Q_{cond} - T_h \sum_i c^i_p S_i}{\sum_i c^i_p \Gamma_i + T_h \sum_i \Gamma_i \frac{dc^i_p}{dT_h}}$$

Here $\Gamma_i = v n_i$ is the flux density of the heavy species i along x, S_i is the volumetric particle source density of this species. The electron density n_e is found from quasineutrality, Z_i is the species charge number, T_e is the temperature of electrons, both T_e and T_h are expressed in energy units. P_{in} is the input power density; $Q^e_{elastic}$ are losses of the electron energy due to their elastic collisions with heavies; $Q^e_{inelastic}$ are the electron energy losses due to inelastic collisions - excitations and chemical reactions; $Q^{e\to h}_{inelastic}$ is the transfer of the electron and potential energy into TR-energy of heavies; Q_{cond} is the radial conduction; c^i_p is the heat capacity (per particle) at constant pressure.

S and Q terms depend on $\{n_i, n_e, T_e, T_h\}$, c^i_p is a function of T_h. $Q^e_{inelastic}$ and $Q^{e\to h}_{inelastic}$ are calculated from the defect of the potential energy in the reaction ΔU = potential energy of products minus potential energy of reagents. For reactions where electrons are involved on both sides ΔU is added to $Q^e_{inelastic}$, otherwise, if no electrons appear in the reaction, ΔU is subtracted from $Q^{e\to h}_{inelastic}$. If electrons appear only on the reactants side (recombination and attachment), then $\Delta U > 0$ is added to $Q^e_{inelastic}$, and $\Delta U < 0$ is subtracted from $Q^{e\to h}_{inelastic}$. The opposite rule is applied if electrons appear only on the products side (reactions with negative ions): $\Delta U < 0$ is added to $Q^e_{inelastic}$, $\Delta U > 0$ is subtracted from $Q^{e\to h}_{inelastic}$. In this treatment the Franck-Condon energy of the products is not taken into account.

$Q^e_{elastic}$ is calculated as described in [6], Eq. (7a), the collision rates are defined in the file [7].

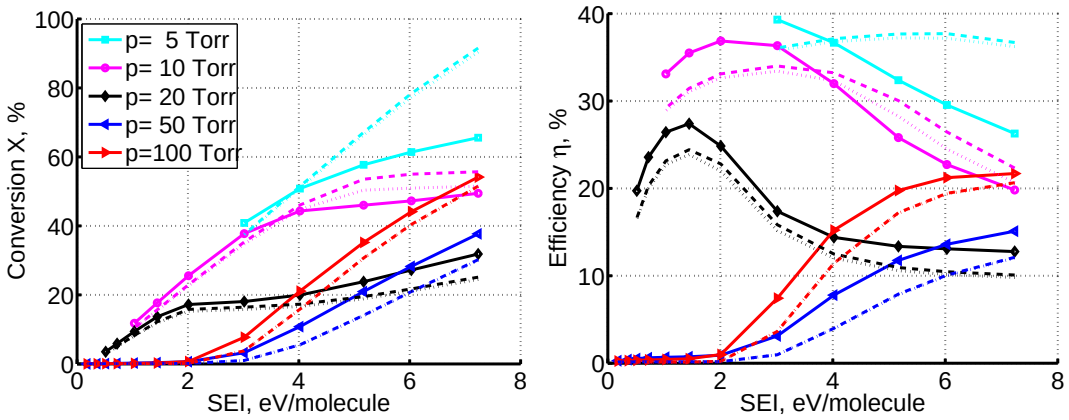

Figure 2: Results of 1D calculations with self-consistent electron density and gas temperature

This term is found to be insignificant. c_p for CO_2 is calculated using Eq. (10) from [5], for all other species c_p=3.5. To calculate Q_{cond} Eq. (6) from [5] is used. Differential equations are integrated by the solver DVODE from the ODEPACK package [8].

The model set-up for calculations corresponds to experiment described in [1], Section c.1). Total power input into discharge 1.4 kW, the discharge zone is 3 cm long and 2 cm in diameter. Initial gas is pure CO_2 with $T_h = T_e$=300 K and Boltzmann distribution of excited states. X and η are calculated at distance 5 m from the inlet. The pressure is varied from 5 to 100 Torr. The particle throughput is varied from 0.05 to 2.0 liter·bar/sec, yielding SIE=0.18..7.2 eV/molecule. Results of calculations are shown in Figure 2.

In the original data-set [7] no reverse reactions are included for the electron impact processes. Absence of de-excitations of the electronically excited states of CO_2, CO and O_2 leads to unrestricted accumulation of those species which is nonphysical. The electron impact rates in [7] are calculated for the Electron Energy Distribution Function (EEDF) taken from the solution of the Boltzmann equation. The EEDF itself is not included in the data set. In order to implement the correction in a simplest way, the rates were first re-calculated for Maxwellian EEDF. The influence on the results is found to be very small (dotted lines in Figure 2). Then the reverse reactions were added to the model. Their rates are calculated from the detailed balance. Solid lines in Figure 2 represent calculations made with Maxwellian EEDF and electronic de-excitations added. Dashed lines show the results obtained with the original model [7].

Qualitative comparison can be made with [1], Fig. 11 and Fig. 15. One can see that the highest η=40 % achieved with the present model is much smaller than expected 80 %. Moreover, the highest values are reached only at small pressures p <10 Torr, there is no maximum at SEI around 0.5..1 eV/molecule and $p \approx$100 Torr as in [1].

Non-uniformity of the discharge zone can lead to concentration of the power input in a region

which is much smaller than that assumed in the model. An example of the solution obtained with the length of discharge zone reduced down to 0.6 cm is shown in Figure 3. The total input power remains the same as above. Comparison with Figure 2 reveals significant increase of η at moderate p, especially for p=50 Torr. Nevertheless, the result remains significantly different from [1].

Dashed line in Figure 3 is the efficiency calculated with total power which goes into chemical transformations $Q_{chem} = P_{in} - Q^{e\to h}_{inelastic} - Q^{e}_{elastic}$ in the nominator. Contrasted with η this quantity shows that at pressures $p \geq 50$ Torr most of Q_{chem} is indeed spent on the target reaction $CO_2 \to CO$. Therefore, since $Q^{e}_{elastic}$ and losses on anharmonicity in Vibrational-Vibrational (VV) exchange are small, the main reason of low efficiency must be Vibrational-Translational (VT) transfer in $Q^{e\to h}_{inelastic}$.

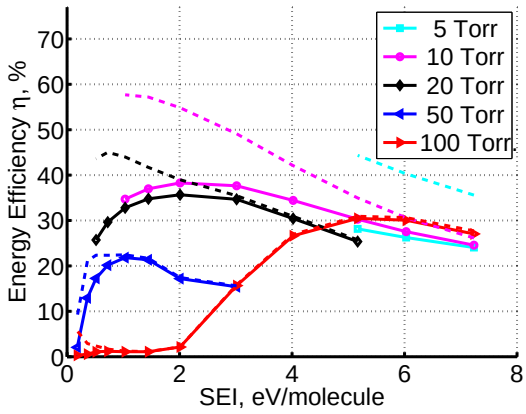

Figure 3: Energy efficiency η calculated with reduced length of the discharge zone

VV and VT rates used here are calculated by applying the scaling relations derived for molecules consisting of two atoms. Distinct from diatomic molecules, the CO_2 molecule has two independent modes of oscillations. Interaction between the two modes leads to broadening of the vibrational energy levels. As discussed in [9] this broadening significantly affects both VV- and VT-rates. Missing of the mode-mixing effect can be the reason of the large discrepancy between the present calculations and the results found in the literature.

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References

[1] V D Rusanov, A A Fridman and G V Sholin, *Sov. Phys.-Usp.* **24** (1981) 447

[2] T Silva et al. *Plasma Sources Sci. Tehnol.* **23** (2014) 025009

[3] A Goede et al. *EPJ Web of Conferences* **79** (2014) 01005

[4] T Kozak and A Bogaerts *Plasma Sources Sci. Technol* **23** (2014) 045004

[5] T Kozak and A Bogaerts *Plasma Sources Sci. Technol* **24** (2015) 015024

[6] P Koelman et al. *Plasma Proceses and Polymers* **14** (2017) 1600155

[7] P Koelman et al., `https://plasimo.phys.tue.nl/resources`

[8] A C Hindmarsh et al., `https://computation.llnl.gov/casc/odepack/`

[9] V D Rusanov, A A Fridman, G V Sholin (1986) Vibrational Kinetics and Reactions of Polyatomic Molecules in Nonequilibrium Systems. In: M Capitelli (eds) *Nonequilibrium Vibrational Kinetics. Topics in Current Physics*, **39**, Springer, Berlin, Heidelberg