Plug flow reactor model of the plasma chemical conversion of CO₂

V Kotov¹ and P M J Koelman²

¹ Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung-Plasmaphysik (IEK-4), Partner of the Trilateral Euregio Cluster (TEC), D-52425 Jülich, Germany
² Eindhoven University of Technology, Department of Applied Physics, PO Box 513, 5600 MB Eindhoven, The Netherlands

E-mail: v.kotov@fz-juelich.de

Received 7 May 2019, revised 4 July 2019
Accepted for publication 31 July 2019
Published 24 September 2019

Abstract

A 1D plug flow model suitable for describing the CO₂ conversion into CO in microwave plasma reactors is proposed. The model is applied together with the Antwerp data set for the CO₂ reaction kinetics to calculate parameter scans for a realistic experimental set up. The energy re-distribution pathways in the model calculations are analyzed. The analysis shows that despite the input power being initially deposited mainly into vibrational states the fast vibrational-translational (VT) transfer leads to dissociation of CO₂ predominantly via the thermal quenching mechanism. Solutions with mitigated VT-losses can be obtained by increasing the specific input power–power per unit volume. In this regime the energy efficiency starts to be constrained by reverse processes.

Supplementary material for this article is available online

Keywords: microwave discharges, mathematical model, 1D model, CO₂ conversion

1. Introduction

Plasma assisted splitting CO₂ → CO + ½O₂ attracted considerable attention in the last decade due to its potentially key role for the electricity to fuel conversion [1]. The interest in this technology is based to a large extent on high energy efficiencies—up to 80%—reportedly obtained in microwave induced discharges in the past [2, 3]. This record high result is not yet fully reproduced in modern day experiments where efficiencies up to 60% have been obtained [4].

It can be expected that careful optimization of the conversion process is required to achieve the highest possible efficiency. Among other methods, predictive mathematical models find broad application for analysis and optimization of experiments. Activities have begun which focus on creating the computational models especially for the CO₂ plasma decomposition. Probably the most detailed plasma chemical model developed for that purpose to date is the state-to-state reaction kinetics of Kozak and Bogaerts also known as ‘Antwerp model’ [5, 6]. In [7, 8] this kinetic scheme is coupled with the gas temperature calculations, and applied as a simplest approximation for describing the microwave conversion.

The model of [7, 8] uses 0D time-dependent formulation. In the present paper the next step towards developing a realistic mathematical description of the microwave CO₂ conversion is presented. The reaction kinetics [5, 6] is implemented in a 1D steady-state plug flow model where electron density, electron and heavy particles temperatures are calculated self-consistently. For slow subsonic flows this approach translates into initial value problem for ordinary differential equations which is numerically as simple to handle as the 0D time-dependent scheme.

The model is applied here for conditions of the experiment described in [2]. The main result of the simulations is that the calculated energy efficiency is far below 80% reported in [2]: 30%–40% at maximum. This outcome agrees qualitatively with previous results obtained with the Antwerp model [5, 7, 8]. It will be shown that despite most of the input
power is initially deposited into vibrational energy of molecules, due to vibrational-translational (VT) processes the conversion of CO$_2$ in the model calculations is activated mainly by the thermal translational-rotational (TR) energy. In the current model the VT-transfer can only be mitigated by increasing the specific input power (with fixed total power) by orders of magnitude. Integral energy analysis of the series of calculations reveals the redistribution of the initial input power over different pathways. The analysis shows, in particular, that presence of the reverse reactions which convert CO back into CO$_2$ may prevent high overall energy efficiency even with mitigated VT-losses.

The rest of the paper is organized as follows. The next section describes the plasma flow model. In section 3 implementation of the reaction kinetics [5, 6, 9] in the present work is described. Section 4 outlines briefly the numerical procedure and some technical aspects of the calculations which may be important for the modeling practitioners. The results of the calculations are presented and analyzed in section 5. The effect of variation of the uncertain model parameters is estimated. Last section summarizes and concludes the main findings.

2. Plug flow reactor model

2.1. Basic equations

The chemical reactor is represented in the model as a long tube with constant cross-section, figure 1. Stationary flow of a multi-component gas along the axis $x$ is considered. The components are heavy species—molecules, atoms, ions—with translational temperature $T_h$ and electrons with temperature $T_e$. Since, in general, electrons have non-Maxwellian velocity distribution, $T_e$ is understood as their mean kinetic energy $<v^2>_e$: $T_e = \frac{3}{2} <v^2>_e$. Here and below the temperatures are always expressed in the units of energy, unless stated otherwise. Velocity distribution of heavy species is assumed to be Maxwellian. Due to their fast relaxation the rotational degrees of freedom have equilibrium distribution with the same Maxwellian. Vibrationally excited states, on the opposite, are included in the model explicitly as separate species.

Standard assumption of the plug flow model is that the fluid is perfectly mixed in the direction perpendicular to the axis. That is, the profiles of both the time averaged axial velocity $v_i$ and density $n_i$ of each component $i$ in the direction perpendicular to the axis are flat. Radial gradients take place only in a thin boundary layer. The same assumption is applied to the temperatures $T_e$ and $T_h$. Perfect mixing also implicitly implies strong friction between species, such that they all have same axial velocity $v_i = v$.

Neglecting viscosity, the axial momentum balance for the sum of all species (including electrons) reads:

$$\frac{d}{dx} \left( \sum_{i=1}^{N} m_i n_i v_i^2 + T_e \sum_{i=1}^{N} n_i + T_e n_e \right) = \frac{d}{dx} \left( 1 + M^2 \right) T_h \sum_{i=1}^{N} n_i + T_e n_e = 0. \quad (1)$$

Here $N_i$ is the total number of heavy species, $m_i$ is the atomic mass of species $i$, $n_e$ is the density of electrons, their inertia is neglected; $M$ is the Mach number:

$$M = \sqrt{\frac{\sum_{i=1}^{N} m_i n_i v_i^2}{T_h \sum_{i=1}^{N} n_i}} = \frac{v}{c_i} = \sqrt{\frac{T_h \sum_{i=1}^{N} n_i}{\sum_{i=1}^{N} m_i n_i}}. \quad (2)$$

The mathematical model is greatly simplified if two extra constraints are taken. First, it is assumed that the degree of ionization stays low and $T_h \sum_{i=1}^{N} n_i \gg T_e n_e$. Second, only slow subsonic flows with $M^2 \ll 1$ are considered. Those two restrictions reduce the momentum balance (1) to conservation of the total static pressure of heavy particles $p$:

$$p = T_h \sum_{i=1}^{N} n_i = \text{const.} \quad (3)$$

Continuity equations are written for the axial particle flux density $\Gamma_i = n_i v_i = n_i v$:

$$\frac{d\Gamma_i}{dx} = S_i (n_e, n_1 \ldots n_N, T_e, T_h) \quad (4)$$

The velocity $v$ is found by multiplying (3) with $v$:

$$v p = T_h \sum_{i=1}^{N} n_i v_i = T_h \sum_{i=1}^{N} \Gamma_i. \quad (5)$$

Thus, when $\Gamma_i$ is known the density $n_i$ is calculated as:

$$n_i = \frac{\Gamma_i}{v} = \frac{\sum_{i=1}^{N} \Gamma_i}{T_h}. \quad (6)$$

The electron density $n_e$ is calculated from quasi-neutrality:

$$n_e = \sum_{i=1}^{N} Z_i n_i, \quad (6)$$

where $Z_i$ is the charge number of the heavy species $i$.

The temperatures $T_h$ and $T_e$ are found from the energy balance equations for the electrons and heavy species:

$$\frac{dq_e}{dx} = Q_{in} - Q_{in} - Q_{\text{elastic}}, \quad (7)$$

$$\frac{dq_h}{dx} = Q_{e-h} + Q_{\text{elastic}} - Q_{\text{wall}} \quad (8)$$

here $Q_{in}$ is the specific input power, $Q_{\text{elastic}}$ is the power lost by free electrons in elastic collisions, $Q_{e-h}$ is the power lost in inelastic collisions; $Q_{in}$ is the electron, potential and vibrational energy transferred into TR energy of heavy particles, $Q_{\text{wall}}$ is the TR energy lost on the walls of the discharge tube related to the unit volume; $q_e$ and $q_h$ are the
axial densities of the heat flux transmitted by the electrons and heavy particles, respectively:

\[ q_e = \frac{5}{2} T_e \sum_{i=1}^{N_e} Z_i \Gamma_i, \] (9)

\[ q_h = T_b \sum_{i=1}^{N} c^i_p \Gamma_i, \] (10)

where \( c^i_p \) is the thermal capacity of the component \( i \) at constant pressure. The condition of ambipolarity—zero electric current—is applied to the axial flux of electrons \( \Gamma_e = \sum_{i=1}^{N} Z_i \Gamma_i \). Note that the coefficient \( \frac{5}{2} \) used here for the enthalpy of free electrons implies nearly Maxwellian velocity distribution.

When \( q_h \) is known (10) can be used to determine \( T_b \). However, since some \( c^i_p \) are functions of \( T_b \), this procedure would lead to a nonlinear equation. For numerical solution it is more convenient to transform (10) into an equation for \( T_b \). For the sake of symmetry the same transformation is applied to the electron energy equation as well. Taking into account (4) derivatives of the heat fluxes (9), (10) are calculated as follows:

\[ \frac{d q_e}{d x} = \frac{5}{2} \frac{d T_e}{d x} \sum_{i=1}^{N_e} Z_i \Gamma_i + \frac{5}{2} T_e \sum_{i=1}^{N_e} Z_i S_i, \] (11)

\[ \frac{d q_h}{d x} = \frac{d T_b}{d x} \left( \sum_{i=1}^{N} c^i_p \Gamma_i + \sum_{i=1}^{N} \frac{d c^i_p}{d T_b} \right) + T_b \sum_{i=1}^{N} c^i_p S_i. \] (12)

The final set of equations which have to be integrated numerically consists of (4) written for each heavy species \( i \) supplemented by (5), (6) and (7), (8) with heat fluxes replaced by temperatures using (11), (12):

\[ \frac{d \Gamma_i}{d x} = S_i, \ n_i = \frac{\Gamma_i}{\sum_{i=1}^{N} \Gamma_i} \frac{p}{T_b}, \ n_e = \frac{\sum_{i=1}^{N} Z_i n_i}{\sum_{i=1}^{N} Z_i \Gamma_i}, \] (13)

\[ \frac{d T_e}{d x} = \frac{Q_{m} - Q_{e}^{\text{inelastic}} - Q_{e}^{\text{elastic}} - \frac{5}{2} T_e \sum_{i=1}^{N} Z_i S_i}{\sum_{i=1}^{N} Z_i \Gamma_i}, \] (14)

\[ \frac{d T_b}{d x} = \frac{Q_{e}^{\text{inelastic}} + Q_{e}^{\text{elastic}} - Q_{\text{wall}}}{\sum_{i=1}^{N} c^i_p \Gamma_i + T_b \sum_{i=1}^{N} \frac{d c^i_p}{d T_b}} + T_b \sum_{i=1}^{N} c^i_p S_i. \] (15)

### 2.2. Heat transfer and heat capacities

The heat transfer term \( Q_{\text{wall}} \) in (15) is calculated by dividing the total heat flux deposited to a wall segment by the volume of the fluid ‘plug’. For a straight cylindrical tube:

\[ Q_{\text{wall}} = \alpha(T_b - T_w) \frac{2\pi R}{\pi R^2} = \alpha(T_b - T_w) \frac{2}{R}, \] (16)

where \( R \) is the tube radius, and \( T_w \) is the temperature of the wall.

The heat transfer coefficient \( \alpha \) is found from an empirical scaling written in terms of the Nusselt \( Nu \), Prandtl \( Pr \) and Reynolds \( Re \) numbers:

\[ Nu = \frac{d \alpha}{\lambda}, \ Pr = \frac{\mu c_p}{\rho \lambda}, \ Re = \frac{v d}{\mu}, \] (17)

where \( d \) is the diameter of the tube, \( \lambda \) is thermal conductivity of the gas mixture, \( \mu \) is its dynamic viscosity, \( \rho \) is its mass density, \( c_p \) is the heat capacity at constant pressure.

The scaling [10], equation (3-3-6), reads:

\[ Nu = 0.023 \cdot Pr^{1/3} \cdot Re^{0.8}. \] (18)

It is plausible to assume that due to the presence of the gas discharge a fully developed turbulent flow is formed in the discharge tube. Therefore, empiric equation (18) obtained for \( Re > 10^4 \) is applied here despite formally the Reynolds numbers in the problems in question are smaller.

Since the way of calculating \( Q_{\text{wall}} \) described above only provides a rough estimate of the wall heat losses, to avoid unnecessary complication the actual composition of the mixture is not taken into account in the calculation of \( \alpha \), and the heat transfer is calculated for pure CO2. It is not to be expected that \( \alpha \) calculated for the mixture will be significantly different because there is only a ±50% variation of \( \mu/\rho \) between CO2, CO and O2, and the variation of \( Pr \) and \( \lambda \) is even smaller. Substituting (17) into (18), and calculating \( \mu \), \( \lambda \) and \( c_p \) of CO2 according to [11] yields the following equation for \( \alpha \):

\[ \alpha = \alpha_T(T_b) \frac{(T_{\text{CO}_2}^{1.9/0.8})}{d^{0.2}}, \] (19)

\[ \alpha_T = 6.74 \times 10^{-21} + 5.17 \times 10^{-20}t - 2.76 \times 10^{-20}t^2 - 5.84 \times 10^{-21}t^3, \ t = \frac{T_b}{1000}. \] (20)

where \( T_{\text{CO}_2}^{1.9/0.8} \) is the initial axial flux density of CO2 at the inlet, expressed in \( 1/(\text{m}^2 \text{s}) \); \( T_b \) is in Kelvin, \( d \) is in meter, the resulting \( \alpha \) is expressed in \( \text{W}/(\text{m}^2 \text{K}) \). The fit for \( \alpha_T \) is derived for the temperature range \( T_b = 200–2000 \text{ K} \). For \( T_b > 2000 \text{ K} \) \( \alpha_T \) at 2000 K is taken. Scripts which were used to produced (20), as well as the code which calculates \( \alpha \) in the model runs are combined in the library ‘CO2 formulary’ [12].

Partial heat capacities \( c^i_p \) of the components which enter (15) are calculated as follows. For all CO2 species, including electronically and vibrationally excited molecules and ions, the fit provided in [7], equation (10), is used. In this fit the vibrational energy is already excluded, avoiding double counting. Calculation of \( c_p \) and \( \frac{d c_p}{d T} \) for CO2 can be found in the same library [12]. For all other species \( c^i_p \) is set to: 2.5 for atoms and atomic ions; 3.5 for diatomic molecules and corresponding ions; 4 for the rest—except CO2.

### 3. Plasma chemical model

#### 3.1. Computer representation

‘Plasma chemical model’ in the context of the present paper is a set of stoichiometric reaction equations and reaction rate coefficients. In a general form the stoichiometric equation
which describes transformations of species in reaction $k$ reads:

$$\sum_{i=1}^{N_i} a_i X_i \rightarrow \sum_{i=1}^{N_i} b_i X_i$$  \hspace{1cm} (21)

here $X_i$ is the chemical species, $a_i$, $b_i$ are stoichiometric coefficients. Reaction equations (21) are translated into source terms in the continuity equations (21):

$$S_i = \sum_{k=1}^{N_e} \left( b_i - a_i \right) R_k \prod_{j=1}^{N_i} \left( n_j \right)^{a_{ij}}$$  \hspace{1cm} (22)

where $N_e$ is the total number of reaction equations, and $R_k$ are the reaction rate coefficients which define the speed of each process.

In the rest of this subsection the technical implementation of the plasma chemistry as it is done in this work is described. The problem is divided into two parts: (i) definition of stoichiometry and calculation of $S_i$; (ii) calculation of the reaction rate coefficients $R_k$. The stoichiometry is defined in the form of a so called ‘reaction network’ which comprises elements, species and equations (21). Elements are introduced to monitor the particle conservation, see section 4.2 below. Data structures for the reaction networks and tools for processing the reaction networks, in particular, the transformation (22) and search functions, are packed in the open source Fortran library REACNET [13].

Rate coefficients $R_k$ are, in general, functions of the plasma and gas parameters $T_e$, $n_e$, $T_n$, $n_n$. There exist no unified and standardized way to define those dependencies in a computer code. Both table interpolations and closed form relations are used. Those latter of various kinds—not only Arrhenius or power law equations. Scaling laws and model calculations ‘on the fly’ can be invoked. Computer programs readily available for plasma chemistry, such as PLASIMO [14] and ZDPlasKin [15], use built in domain specific languages to program the calculations.

In the present work it was decided to program the calculation of the rate coefficients directly in Fortran, without introducing any extra language layer. The corresponding Fortran subroutine is stored in the run folder and is linked to the main program at run time. Flow chart of a modeling run is shown in figure 2. In this diagram plasmachem.f90 is the Fortran file which acts as an input file. This file is case specific and is adjusted to the reaction network defined in plasmachem.rn. In addition, if calculations of some rate coefficients use tables, then those tables are stored in plasmachem.tb. Subroutines from plasmachem.f90 are called in the main program plug_flow.f90. Both the case specific and the main parts of the program use generic subroutines and functions collected in the library REACNET.

3.2. ‘Minimal model’ of the inelastic energy transfer

The basic quantity used for calculation of $Q^{c\rightarrow h}_{\text{inelastic}}$ and $Q^{c\rightarrow h}_{\text{inelastic}}$ is the increase of potential energy in reaction $k$, see (21):

$$\Delta E_k = \sum_{i=1}^{N_e} b_i E_i - \sum_{i=1}^{N_e} a_i E_i,$$  \hspace{1cm} (23)

where $E_i$ is the potential energy of species $i$. Here and below ‘potential energy’ also includes the energy of vibrational excitations. The total rate of the potential energy increase is found by multiplying $\Delta E_k$ with collision rate:

$$S^k = R_k \prod_{j=1}^{N_e} \left( n_j \right)^{a_{ij}}.$$  \hspace{1cm} (24)

If electrons appear on both sides of the stoichiometric equation, and $\Delta E_k > 0$, then it is assumed that free electrons lose exactly this portion of their kinetic energy. Otherwise, when $\Delta E_k < 0$, the reduction of potential energy goes into kinetic energy of free electrons. In both cases $S^k \Delta E_k$ is added to $Q^{c\rightarrow h}_{\text{inelastic}}$, and $Q^{c\rightarrow h}_{\text{inelastic}}$ receives no contribution from reaction $k$. It is readily seen that in this approximation the increase of the kinetic energy of heavy products in the electron impact dissociation processes due to Franck–Condon effect is not taken into account. That is, for those processes this model only provides a lower bound of the electron energy losses.

Apparently, when $\Delta E_k > 0$, and there are no electrons on the reactants (left hand) side of the reaction equation the potential energy can only increase due to reduction of the TR-energy of heavy particles. For such reactions $Q^{c\rightarrow h}_{\text{inelastic}}$ is not updated, and $Q^{c\rightarrow h}_{\text{inelastic}}$ is reduced by $S^k \Delta E_k$. A similar approach is used when $\Delta E_k < 0$, and there are no electrons on the products (right-hand) side. Since the potential energy cannot transfer into kinetic energy of electrons any more, $\Delta E_k$ can only go into TR-energy. Again, $S^k \Delta E_k$ is subtracted from $Q^{c\rightarrow h}_{\text{inelastic}}$. $Q^{c\rightarrow h}_{\text{inelastic}}$ is not modified. One further correction is required in this case. Since free electrons are lost in the reaction, their kinetic energy should also disappear from the collective thermal energy of the electron gas. To take this into account the quantity $N_e^2 \frac{2}{5} T_e S^k$ is added to $Q^{c\rightarrow h}_{\text{inelastic}}$, where $N_e^2$ is the number of electrons on the reactants side. This kinetic energy can only go into TR-energy, therefore, $N_e^2 \frac{2}{5} T_e S^k$ is also added to $Q^{c\rightarrow h}_{\text{inelastic}}$. Obviously, formal rules of this paragraph are directly applicable to reactions which involve no electrons at all.

3.3. ‘Antwerp model’ of the CO$_2$ plasma chemistry

The plasma chemical model applied here was originally developed by Kozak and Bogaerts [5], and then updated by Koelman et al [6]. In internal and private communications this model is referred to as ‘Antwerp model’ or ‘Kozak–Bogaerts–Koelman’ model. The implementation in the present work is based on the published PLASIMO input file [9] which was translated into Fortran and re-implemented with REACNET (see section 3.1).
Some technical mistakes found in the original version of the input file had to be corrected. In particular, reduction of the activation energy of reactions N1, N2, N5 for vibrationally excited reactants effectively was not taken into account. Meanwhile the corrected input can be found on the updated web-page [9]. The corrections were found to have negligible impact on the dielectric barrier discharge test case shown in [6], but are thought to be of paramount importance for conversion in microwave discharges.

Detailed survey of the model [6, 9] also showed that it did not contain processes reverse to the electron impact excitations. For electronically excited states of CO₂, CO and O₂ the electron impact de-excitation is the main process which depopulates those states. In the absence of de-excitation their population becomes unrealistically high, and substantial amount of potential energy which could be otherwise spent for the chemical transformations is accumulated in those states. This nonphysical artifact also had to be removed.

In the original model [6, 9] the rate coefficients were calculated for a non-Maxwellian electron energy distribution function (EEDF), and tabulated as functions of Te = \( \frac{2}{3} (e_i) \). Unfortunately, the EEDFs for which the calculations were made are not stored in the model archive. At the same time, there are indications that in the microwave discharges EEDF is close to Maxwellian [16]. Taking into account this observation, in order to implement the required correction in the most simple way it was decided to switch to Maxwellian EEDF. The rate coefficients of the electron impact reactions were re-calculated using cross-sections from [9] and scaling laws described in [5, 6]. In addition, since experience has shown that the electron energy losses due to elastic collisions are very small, the term Q_{plastic} in (14), (15) is set to zero.

After that the de-excitations of the electron impact reactions were added. The final chemical model which was applied for calculations in the present work also contains some further less significant modifications. In particular, cross-sections of the multi-quantum electron impact vibrational excitation of CO from ground state were taken directly from [17] (Phelps database) rather than calculating them by up-scaling the cross-section of the single-quantum process.

Technical benchmarks and all step-by-step modifications applied to the original ‘Kozak–Bogaerts–Koelman’ model [6, 9] are described in supplemental material is available online at stacks.iop.org/PSST/28/095002/mmedia, where the influence of each step on the solution is evaluated as well. In particular, plots titled ‘Model 5 versus Model 4’ demonstrate that with exception of Te the impact of the assumption of Maxwellian EEDF on the model output is very small. The reference plasma chemical model in REACNET format can be found here [18].

4. Numerical procedure

Solver DVODE from the package ODEPACK is used for numerical integration of the set of equations (13)–(15). This solver is developed especially for stiff problems of chemical kinetics. It uses backward differential formulas for numerical integration of ODEs, see [19]. In DVODE the variable coefficient version of this algorithm is applied which was developed for better handling of sharp variations in the coefficients and solutions [20]. Same solver is normally applied in PLASIMO [14] and with ZDPlasKin [15].

The source code of the ODE solver is downloaded from [21]. In all calculations the internally generated Jacobian in Newtonian solver is used (option MF = 22). Both relative and absolute accuracy is set to 10^-8 (ATOL = RTOL = 1 × 10^-8). For most model runs the whole code, figure 2, is compiled with double precision. It was found that in some cases the calculations do not converge unless the code is compiled with quadruple precision—128 bytes for one floating point number. (In ifort compiler, version 18.0.3, this is options -real-size 128 -double-size 128.) The increased precision was most probably required due to occurrence of small, but significant differences of very large numbers in the particle source terms (22).

As the concentration of electrons is reduced to a very small value, T_e calculated by numerical integration of (14) can get smaller than T_h, and even become negative. Negative T_e in turn, may cause floating point exception when the rate coefficients R_k are calculated because they are defined only for positive temperatures. This issue is eliminated, as in [6], by calculating R_k for the so called ‘measured temperature’ = max(T_e, T_h) instead of T_e.

4.1. Stopping condition

The main goal of the present paper is to investigate the conversion of CO₂ into CO. Therefore, to avoid unnecessary long computations not the full thermodynamic equilibrium, but rather saturation of the CO flux \( \Gamma^{\text{CO}} \) is chosen as the stopping condition for the integration of (13)–(15) over x. Here \( \Gamma^{\text{CO}} \) is the total flux of all states of CO. Mathematically this condition is expressed in terms of the exponential relaxation length:

\[
\Lambda^{-1} = \left| \frac{d \ln \Gamma^{\text{CO}}}{dx} \right| = \left| \frac{1}{\Gamma^{\text{CO}}} \frac{d \Gamma^{\text{CO}}}{dx} \right|.
\]  

Large \( \Lambda \) implies small variation of ln(\( \Gamma^{\text{CO}} \)) over long distance x. If \( \Gamma^{\text{CO}}(x) \approx \exp \left( -\frac{x}{\Lambda} \right) \), then \( \Lambda \) defined by (25) equals to \( \lambda \).

In the numerical procedure the integration pauses at certain points \( x_k \), and the following condition is checked:

\[
\Lambda \approx \left| \frac{1}{\Gamma^{\text{CO}}} \frac{\Gamma^{\text{CO}} - \Gamma^{\text{CO}}_{k-1}}{x_k - x_{k-1}} \right| > \Lambda_{\text{min}},
\]  

where \( k - 1 \) is the previous check point, and \( \Lambda_{\text{min}} \) is the prescribed minimum relaxation length.

Experience has shown that fulfillment of (26) only in the last check point does not guarantee good results. For some combinations of the input parameters there is a non-negligible difference between solutions obtained with \( \Lambda_{\text{min}} = 1 \times 10^6 \text{ m} \) and \( \Lambda_{\text{min}} = 1 \times 10^8 \text{ m} \). Further increase of the relaxation length may lead to saturation of the results with respect to \( \Lambda_{\text{min}} \), but the computational time increases drastically. The
reason of the problem is thought to be local maxima or 
minima of $\Gamma_{\text{CO}}(x)$ where variation of $\Gamma_{\text{CO}}$ between $x_{k-1}$ and $x_k$ gets locally small. To work around this issue the integration stops only when the condition (26) is fulfilled in $N_i > 1$ check points in a row. $\Delta_{\text{min}} = 1 \times 10^6 \text{m}$ and $N_i = 6$ were used for the calculations presented in section 5 below. Tests have confirmed that with this method the increase of $\Delta_{\text{min}}$ does not lead to any non-negligible modification of the solution. Stopping criterion (26) is ignored if $x$ is smaller than the length of the discharge zone $l$.

As explained in section 2, the present plug flow model is only applicable for small Mach numbers $M$. That is, the model runs where large $M$ occur have to be discarded as invalid. For not to lose the computing time in obsolete runs, such simulations are stopped and eliminated automatically. The Mach number (2) is calculated at each check point $x_k$. If $M > M_{\text{max}} = 0.3$, then the integration stops immediately, and the run is discarded.

### 4.2. Run time checks

In order to ensure that the results of computations do not contain crude mistakes and internally consistent, in each model run the fulfillment of conservation laws is checked automatically.

The most basic of them is the particle conservation. Conserved quantity is the element flux:

$$
\Gamma^i = \sum_{j=1}^{N_i} N_j \Gamma^i_j, \quad (27)
$$

where $\alpha$ is the index of an element, $N^i_j$ is the number of particles of the element $\alpha$ in species $i$. ‘Elements’ are constituents of the species which do not change in the course of chemical transformations: atomic nuclei and electrons. The conservation check is passed when the following inequality is fulfilled:

$$
\frac{[\Gamma^i_{\text{in}} - \Gamma^i_{\text{out}}]}{[\Gamma^i_{\text{in}}]} < \epsilon_{\text{part}}, \quad (28)
$$

Here and below the superscript in stands for quantity at inlet, $x = 0$, and the superscript out stands for the point $x_{\text{end}}$ where integration stops—‘outlet’. The tolerance parameter was set to $\epsilon_{\text{part}} = 1 \times 10^{-10}$.

The global energy balance is written separately for:

(i) kinetic energy of free electrons; (ii) TR-energy of heavy species; (iii) potential and vibrational energy. Below those latter are combined and called ‘potential energy’. Equations for electrons and heavy species are obtained by integrating (7) and (8) over $x$ from 0 to $x_{\text{end}}$:

$$
q_e^{\text{out}} - q_e^{\text{in}} = P_{\text{in}} - P_{\text{elastic}} - P_{\text{elastic}}, \quad (29)
$$

$$
q_h^{\text{out}} - q_h^{\text{in}} = P_{e^{\text{--h}}} - P_{\text{elastic}} - P_{\text{wall}}, \quad (30)
$$

The $P$-terms are integrals of the corresponding $Q$-terms:

$$
P = \int_0^{x_{\text{end}}} Q\,dx. \quad (31)
$$

The balance of potential energy readily follows from the definition of $Q_{\text{elastic}}$ and $Q_{\text{inelastic}}$:

$$
q_{\text{pot}}^{\text{out}} - q_{\text{pot}}^{\text{in}} = P_e^{\text{--h}} - P_{e^{\text{--h}}} + P_{\text{elastic}} - P_{\text{elastic}} = \sum_{i=1}^{N} E_i \Gamma^i. \quad (32)
$$

Equations (29)-(32) lead to the conditions which have to be fulfilled to pass the global energy balance check:

$$
\begin{align*}
\left| \frac{q_{\text{in}}^{\text{in}} - q_e^{\text{out}} + P_{\text{in}} - P_{\text{elastic}} - P_{\text{elastic}}}{P_{\text{in}}} \right| & < \epsilon_{\text{energy}}, \quad (33) \\
\left| \frac{q_{\text{in}}^{\text{h}} - q_h^{\text{out}} + P_{e^{\text{--h}}} + P_{\text{elastic}} - P_{\text{wall}}}{P_{\text{in}}} \right| & < \epsilon_{\text{energy}}, \quad (34) \\
\left| \frac{q_{\text{pot}}^{\text{out}} - q_{\text{pot}}^{\text{in}} + P_{e^{\text{--h}}} - P_{\text{elastic}} - P_{\text{elastic}}}{P_{\text{in}}} \right| & < \epsilon_{\text{energy}}. \quad (35)
\end{align*}
$$

Accurate calculation of integrals (31) would have to be implemented inside the ODE solver. Since this was technically too complex, a simple provisional solution is taken. The solver pauses at selected nodes $x_k$—same as nodes which are used to check the stopping criterion in the previous subsection. The information is collected at the check points, and the integrals are calculated with trapezoidal method. The following grid step $\Delta x = x_k - x_{k-1}$ was applied: for $x < 2l$ ($l$ is the length of the discharge zone) $\Delta x = l/3 \times 10^6$; for $x \geq 2l\Delta x = 1 \times 10^4$. On this grid it was possible to fulfill (33)-(35) with $\epsilon_{\text{energy}} = 1 \times 10^{-4}$.

### 5. Results of calculations

#### 5.1. Reference model

The model set up corresponds to the experiment described in section 2.3 of [2]. Total input power $P_{\text{in}} = 1.4 \text{ kW}$, diameter of the discharge tube $d = 3.8 \text{ cm}$, length of the discharge zone $l = 3 \text{ cm}$, see figure 1. The initial gas at $x = 0$ is pure CO2 with $T_e = T_h = 300 \text{ K}$, and Boltzmann distribution of excited states. Scans over the gas pressure $p$ and the specific energy input (SEI) per CO2 molecule are calculated. SEI is controlled by the initial particle flux density at $x = 0$ as follows:

$$
\Gamma_{\text{CO2}}(x = 0) = \frac{P_{\text{in}}}{\text{SEI}} \cdot A = \frac{\pi d^2}{4}. \quad (36)
$$

SEI in the denominator must be expressed in the same energy units as $P_{\text{in}}$. The plasma chemical model [18] is used in the reference calculations.

The resulting scans of the conversion rate $X$ and the energy efficiency $\eta$ are presented in figure 3. The conversion rate is defined here as:

$$
X = \frac{\Gamma_{\text{CO}}(x = x_{\text{end}})}{\Gamma_{\text{CO2}}(x = 0)}, \quad (37)
$$

where $\Gamma_{\text{CO}}(x = x_{\text{end}})$ is the total flux of all states of CO taken at the end of integration. The energy efficiency $\eta$ is defined as follows:

$$
\eta = \frac{2.93 \text{ eV}}{\text{SEI}} \cdot X. \quad (38)
$$

here 2.93 eV is the ideal cost of producing one CO molecule.
Distinct from the results reported in [2, 3], the calculated \( \eta \) does not exceed 40%. Moreover, its maximum is achieved at \( p = 20 \) Torr, and not at pressures around 100 Torr. To analyze the factors which reduce the energy efficiency we have to look closer at the dissociation mechanism described in [2, 3]. This mechanism consists of the following steps. First, free electrons spend most of their energy on excitation of vibrational states of CO\(_2\), predominantly on the excitation of asymmetric mode. Second, population of the high vibrationally excited states of CO\(_2\) due to vibrational–vibrational (VV) exchange over the asymmetric mode. Finally, fast dissociation of the molecules with high vibrational energy.

In figure 4 the inelastic electron energy losses in the model calculations are plotted. The electron temperature in the discharge zone is around 2 eV, see figure 7(b) below (dashed lines). Figure 4(a) shows, that at SEI < 3 eV more than 80% of the input power \( P_{in} \) is deposited into vibrational energy of CO\(_2\), mostly into asymmetric modes. This fraction is reduced at higher SEI and \( p > 20 \) Torr. The rest of \( P_{in} \) which does not go into vibrational modes of CO\(_2\) at SEI \( \geq 3 \) eV mainly lands in vibrational excitations of the conversion product CO, figure 4(b). Close look at the vibrational kinetics of the model, see [5], suggests that there is a large probability of the VV-energy exchange between CO and the asymmetric vibrations of CO\(_2\), whereas VT-rates of CO are very low. That is, the energy invested into vibrational states of CO eventually deposits into asymmetric modes of CO\(_2\) as well. Excitation of the oxygen O\(_2\) vibrations by
Thermal activation of the vibrational states of O$_2$ by the reverse molecules indeed dominates the losses of vibrational energy. Electron impact plays a minor role in the primary redistribution of $P_{in}$ because of highly resonance cross-sections, see [17], Phelps database. In total, as one can see from figure 4(b), at $p \geq 20$ Torr more than 90% of the primary energy of free electrons is deposited into vibrational energy of molecules.

That is, the first condition required for realization of the vibrational CO$_2$ conversion mechanism is fulfilled. However, the resulting total energy efficiency $\eta$, figure 3(b), is apparently much lower than the fraction of $P_{in}$ deposited initially into vibrational states. First reason of that are the losses of vibrational energy in VT-processes. In figure 5(a) contribution to the integral $P_{inelastic}$ from all VT as well as VV processes is shown. Those are all processes of the group 'V' in [5, 6]. Dashed lines show only the losses due to VV-exchange between asymmetric and symmetric modes of CO$_2$ and subsequent VT-losses from symmetric modes—processes V1, V2 and V7 in the full kinetic scheme [5, 6]. The net effect of both the direct and reverse processes is plotted. It is readily seen that when SEI < 3–4 eV the net VT-losses are relatively small only at very low pressures $p < 10$ Torr. At pressures $20 \leq p \leq 100$ Torr this term is always larger than 80% of $P_{in}$ and VT-transfer from CO$_2$ molecules indeed dominates the losses of vibrational energy. Thermal activation of the vibrational states of O$_2$ by the reverse VT-processes leads to negative VT-losses—net transfer of TR-energy into vibrational energy. This is the reason why in some cases the sum over all VT- and VV- processes in figure 4(a) is smaller than the losses due to VT-processes with CO$_2$ only. Intensive VT-transfer manifests itself in strong increase of the TR-temperature of heavy particles, see figure 6(b) below.

At high SEI approaching 6 eV the net VT-losses appear to reduce, for the highest pressure $p = 100$ Torr this term even formally goes to zero. In this parameter range the net losses of vibrational energy start to be dominated by the chemical reactions rather than VT-transfer. Contribution of the chemical reactions—processes of the group 'N' in [5, 6] into $P_{inelastic}$ is shown in figure 5(b). The most important reactions are listed in table 1. The dashed lines in the figure show contribution of reactions N1, N2 and their reverse processes N4, N5 only. One can see that at $p \geq 10$ Torr those reactions are dominant in the integral energy balance. Negative values of the energy exchange term stand for the net transfer of TR-energy into chemical potential energy. That is, for thermal activation of the dissociation processes rather than activation by vibrational energy. This result could be expected already from the observed strong temperature increase. Large positive values for $p = 100$ Torr reflect the net transfer of vibrational energy into TR-energy mentioned above. Vibrational energy is lost in exothermic chemical reactions when reactants are vibrationally excited, at first place in reactions N4, N5.

It should be clear that formal dominance of the chemical mechanism of vibrational energy losses does not imply that under those conditions VT-losses are negligible. It implies merely that direct VT energy transfer is compensated by the reverse processes rather than by the VT-losses, and the net flux of vibrational energy towards TR-energy is sustained by the chemical reactions. In the model calculations with reactions N4, N5 switched off the VT + VV contribution gets >80% in the whole SEI range, see figures 8(c), (f) below. Of note also, that the energy exchange pathways as they appear at high $p$ and SEI could be an artifact of the chemical model. In the applied chemical kinetics scheme it is assumed that the products of chemical reactions ('N'-processes) are always in ground state. That is, the transfer of the chemical potential energy back into vibrational energy is artificially blocked.

To summarize, in the present model most of the energy invested into the electron heating is, indeed, deposited into
vibrational energy of CO2. The first condition of the vibrational mechanism of the CO2 conversion is fulfilled. However, the initial vibrational energy eventually transfers mostly into TR-energy of the gas. Subsequently, relatively large X and η seen in figure 3 at SEI > 2 eV and p > 10 Torr are mainly the result of the thermal quenching mechanism, rather than the non-thermal excitation of vibrational states.

5.2. Variation of input parameters

Two particular issues where 1D model faces its limits are non-uniformity of the discharge and heat transfer in a 3D reacting flow. In this subsection the influence of those uncertainties on the modeling results is estimated. The presence of a non-homogeneous discharge with steep gradients can increase the level of turbulence in the gas flow. If this happens the radial heat transfer to the walls will be significantly intensified, and (19) will underestimate the heat flux.

To find out which consequence the heat transfer enhancement may have on the conversion process a series of calculations was made with heat transfer coefficient α (19) multiplied by a factor 10. The results are presented in figure 6. The impact on the maximum gas temperature in the reacting flow appears to be relatively weak, figure 6(b). The effect manifests itself mainly in the shift of the η maxima towards higher SEI for p > 20 Torr. The η peak values themselves experience a moderate reduction.

Another possible consequence of the discharge non-uniformity, in particular, of radial contraction of the plasma zone, is much larger local specific input power \( P_{in} \) than that assumed for a homogeneous discharge. To mimic this situation in the 1D model the length of the discharge zone \( l \) is reduced while keeping the total input power \( P_{in} \) fixed. The results obtained with \( l \) reduced to 0.3 cm from the reference value 3 cm are shown in figure 7. Subsequently, the specific input power \( P_{in} = 1.3 \times 10^6 \text{ W m}^{-3} \) of the reference model is increased by a factor of 10. The most prominent consequence of the higher discharge intensity is strong—by an order of magnitude—increase of the electron density \( n_e \) at all pressures, figure 7(c). The maximum electron temperature \( T_e^{max} \) is increased as well, figure 7(c), but only at low pressures \( p < 20 \text{ Torr} \), whereas at higher pressures \( T_e^{max} \) stays almost unchanged.

Increased electron density in the discharge zone increases the number density of the initial vibrationally excited molecules. Roughly speaking, the rate of VV-transfer is proportional to the square of this density, while the rate of VT-transfer is linearly proportional to this density. Therefore, one may expect that the increased \( n_e \) will speed up the VV-processes to larger extent than VT, thus increasing the utilization of vibrational energy for dissociation from the high vibrational states. Figure 7(a) demonstrates that this beneficial impact of high \( n_e \) on η is observed in the model, but only in a very limited parameter range. Significant effect is only seen for \( p = 10 \), 20 Torr and SEI < 4 eV, but at higher pressures the efficiency does not change at all.

The result is explained in figure 8 where the same contributions to the integral \( P_{inelastic}^{\alpha} \), as in figure 5 above are plotted for several pressures \( p \). At pressure \( p = 20 \text{ Torr} \) the VT-losses are indeed significantly reduced with increased \( Q_{in} \).
This effect is partly compensated by losses in chemical reactions, but does not cancel out. At higher pressures the net VT-transfer does not reduce compared to the reference case. As a result, intensification of the electron impact excitation does not improve $\eta$ because most of vibrational energy is still lost into TR-energy. At $p = 50, 100$ Torr the dissociation of CO$_2$ eventually proceed via thermal quenching mechanism, same as in the reference calculations. The feature at $p = 100$ Torr and SEI $\lesssim 3$ eV was already discussed in the previous subsection.

To find out if VT-losses can be affected at $p > 20$ Torr as well by further increasing $Q_{\text{in}}$, the calculations were repeated with $l = 3 \times 10^{-2}$ cm. Indeed, one can see that at $p = 20$ Torr the VT-transfer is further reduced, there is a pronounced effect for $p = 50$ Torr, and less pronounced effect for $p = 100$ Torr. In all cases the net losses of vibrational energy in chemical reactions are increased.

6. Summary

The ‘Antwerp model’ [5–7] of the CO$_2$ plasma chemical conversion is extended by a 1D stationary subsonic plug flow model applicable to microwave reactors. Calculations have been performed for conditions of the experiment described by Rusanov et al [2, 3]. The maximum calculated energy efficiency $\eta$ obtained with the present model is 40% at pressure $p = 20$ Torr. This figure is much smaller than $\eta = 80\%$ (at $p \approx 100$ Torr) reported in [2, 3].

Analysis have shown that in the numerical simulations more than 80% of the input power $P_{\text{in}}$ invested into electrons is always deposited into vibrational states of CO$_2$ and CO. Moreover, when SEI per one CO$_2$ molecule is small, SEI $< 3$ eV, more than 80% of $P_{\text{in}}$ goes specifically into excitation of the asymmetric modes of CO$_2$. Nevertheless, at $p \geq 20$ Torr most of this vibrational energy is eventually
disposed into heat via VT processes. As a result, the model solution indicates an increase of the TR gas temperature well above 1000 K. The dissociation of CO2 in the model mainly takes place due to thermal quenching mechanism, rather than due to activation by vibrational energy suggested in [2, 3].

Solutions with mitigated VT-transfer can be obtained when the specific input power into discharge is increased—by reducing the length of the discharge zone while keeping the total input power fixed. However, lower VT-losses do not automatically mean high $\eta$ because of vibrational and potential energy losses in reverse reactions—recombination of CO back into CO2.

**ORCID iDs**

V Kotov 🏳️‍🌈 https://orcid.org/0000-0003-3832-4257

P M J Koelman 🏳️‍🌈 https://orcid.org/0000-0002-9987-6875

**References**

[1] Snoeckx R and Bogaerts A 2017 *Chem. Soc. Rev.* **46** 5805
[2] Rusanov V D, Fridman A A and Sholun G V 1981 *Sov. Phys.—Usp.* **24** 447
[3] Fridman A A 2008 *Plasma Chemistry* (Cambridge: Cambridge University Press)
[4] Goede A et al 2014 *EPJ Web Conf.* **79** 01005
[5] Kozak T and Bogaerts A 2014 *Plasma Sources Sci. Technol.* **23** 045004
[6] Koelman P et al 2017 *Plasma Process. Polym.* **14** 1600155
[7] Kozak T and Bogaerts A 2015 *Plasma Sources Sci. Technol.* **24** 015024
[8] Berthelot A and Bogaerts A 2017 *J. Phys. Chem.* **121** 8236
[9] Koelman P et al 2017 *Plasma Sources Sci. Technol.* **23** 045004
[10] Lykov A V 1978 *Heat and Mass Transfer. Handbook* (Moscow: Energia) in Russian
[11] Vesovic S et al 1990 *J. Phys. Chem. Ref. Data* **19** 769
[12] https://jugit.fz-juelich.de/v.kotov/co2-formulary.git
[13] https://jugit.fz-juelich.de/v.kotov/reaflow.git
[14] van Dijk J et al 2009 *J. Phys. D: Appl. Phys.* **42** 194012
[15] Pancheshnyi S, Eismann B, Hagelaar G J M and Pitchford L C
[16] Computer code ZDPlasKin https://zdplaskin.laplace.univ-tlse.fr
[17] The Plasma Data Exchange Project https://fr.lxcat.net
[18] https://jugit.fz-juelich.de/reaflow/7
[19] Byrne G D and Hindmarsh A C 1987 *J. Comput. Phys.* **70** 1
[20] Brown P N, Byrne G D and Hindmarsh A C 1989 *SIAM J. Sci. Stat. Comput.* **10** 1038
[21] https://computation.llnl.gov/casc/odepack/

**Figure 8.** Total losses of vibrational and potential energy, same quantities as in figure 5, calculated with different specific energy input $Q_in$—different length of the discharge zone $l$. Dashed lines are the calculations made without reactions N4, N5.