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# Coupled multi-dimensional modelling of warm plasmas: Application and validation for an atmospheric pressure glow discharge in $CO_2/CH_4/O_2$



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#### ABSTRACT

To support experimental research into gas conversion by warm plasmas, models should be developed to explain the experimental observations. These models need to describe all physical and chemical plasma properties in a coupled way. In this paper, we present a modelling approach to solve the complete set of assumed relevant equations, including gas flow, heat balance and species transport, coupled with a rather extensive chemistry set, consisting of 21 species, obtained by reduction of a more detailed chemistry set, consisting of 41 species. We apply this model to study the combined  $CO_2$  and  $CH_4$  conversion in the presence of  $O_2$ , in a direct current atmospheric pressure glow discharge. Our model can predict the experimental trends, and can explain why higher  $O_2$  fractions result in higher  $CH_4$  conversion, namely due to the higher gas temperature, rather than just by additional chemical reactions. Indeed, our model predicts that when more  $O_2$  is added, the energy required to reach any set temperature (i.e., the enthalpy) drops, allowing the system to reach higher temperatures with similar amounts of energy. This is in turn related to the higher  $H_2O$  fraction and lower  $H_2$  fraction formed in the plasma, as demonstrated by our model. Altogether, our new self-consistent model can capture the main physics and chemistry occurring in this warm plasma, which is an important step towards predictive modelling for plasma-based gas conversion.

#### 1. Introduction

Plasma-based gas conversion is gaining increasing interest, due to the synergy between renewable energy sources and the electrically driven technology [1,2]. To support the experiments, detailed plasma chemistry models have been developed, using a global/zerodimensional (0D) modelling approach [3–6]. These type of models allow for a fast calculation of the densities of plasma species as a function of time, and due to their computational efficiency, they have been extensively used in the field. However, global models cannot describe plasma reactors, which operate outside the range of validity of the analytical expressions describing the extra dimensions. Viegas et al. compared the 0D and 1D approach for modelling a low pressure oxygen plasma [7]. Their work shows that deviation between the models appears already at 10 Torr, due to the plasma contraction, and even below 10 Torr for narrower tubes. The classical approximation employed in the popular plasma chemical kinetics codes, like ZDPlasKin, assumes that the radial temperature profile is parabolic, which at higher pressures (even above 10 Torr) becomes invalid. In addition, the radial dependence of the thermal conductivity on the plasma composition makes the problem even more strongly dependent on the spatial parameters of the gas. When a swirling flow is employed, the classical 1D approximations also become questionable, due to the lack of analytical expressions describing the flow behaviour in such systems. In order to accurately describe the behaviour of a plasma and its afterglow in a non-uniform geometry with swirling flow, the multi-dimensionality of the system has to be taken into account, together with all relevant physics and chemistry.

Multi-dimensional models are being developed to solve these issues, by self-consistently calculating the temperature profile and electrical properties from an input power, or by employing circuit models, which also model the power supply sustaining the plasma [8,9]. A 2D drift-diffusion model for plasma-assisted combustion of CH<sub>4</sub> at atmospheric pressure was built by Takana et al. [10] Quasineutral and nonquasineutral gliding arc models have been built by Kolev et al. [11] 2D axisymmetric glow and arc discharges have been modelled in a nitrogen flow by Tsonev et al. [12] A major drawback is the considerable computational cost, making it impossible to include a detailed chemistry. Deng et al. built a plasma-assisted combustion model for CH<sub>4</sub>, weakly coupling the electric field, heat transfer and turbulent flow, while using a strongly reduced chemistry set, as describing the full chemical mechanism is unfeasible [13]. Other ways to circumvent this

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problem is by solving the chemistry decoupled from the other (heat and flow) equations [8,14] or by assuming a local chemical equilibrium (LCE) approximation, where chemical equilibrium is instantly reached at a given temperature and no macroscopic fluxes are present [15,16]. We will illustrate in this paper that these approaches are often not valid, and that there is a need for more accurate multi-dimensional models.

The gas conversion in warm plasmas, e.g. high current gliding arc (GA), microwave (MW) and atmospheric pressure glow discharge (APGD) plasmas, is thermally driven [8,14,15,17,18]. Even though the gas temperature of these low-current high-voltage plasmas reaches a few thousand Kelvin, the electron temperature is still higher; hence the plasma is not a thermal plasma. On the other hand, the gas temperature is much higher than for non-thermal plasmas (which are close to room temperature). Therefore, these plasmas are typically divided into "warm plasmas". The most important chemistry, which changes the gas composition in a notable way that can be experimentally validated, can be described using a kinetics scheme only dependent on translational temperature and pressure. This allows for the chemistry to be realistically described using a thermal kinetics model, excluding the effect of the electrons on the gas composition. The electrons in the plasma are then considered to only heat the gas, which is described in the model as a non-solid heat source at the position of the plasma.

Ideally, plasma reactors should be described using a 3D coupled model, solving gas flow, heat transfer, species transport and chemistry, the Poisson and current conservation equations. However, the computational cost of mesh-converged calculations makes such models unfeasible [19]. In this paper, we therefore propose a 2D axisymmetric model to describe 3D plasma reactors, limiting the number of mesh cells needed, to effectively reduce the computational costs. Furthermore, we reduce a complex thermal chemistry set using a sensitivity analysis, to allow a coupled implementation in the 2D axisymmetric model, for a more correct description of the interactions between the chemistry, gas flow and heat equations than the model approaches previously considered [8,9]. The Poisson and current conservation equations are not solved, because as mentioned above, in warm plasmas, where thermal chemistry is dominant, we can use a heat source to describe the gas heating from the plasma. This is indeed a valid approach, considering a (known) electron density profile and assuming the electron temperature to be equal to the gas temperature [20].

The main improvement of our model is that we include the selfconsistent computation of the heat capacity and thermal conductivity of the gas mixture/plasma in a 2D swirling flow. Indeed, the gas flow velocity and diffusion do affect the thermodynamic properties of the system and LCE is not reached. Comparison with experimental results shows that this modelling approach is necessary to correctly describe the behaviour in a real plasma reactor.

As a case study, we apply these coupled models to simulate the effect of  $O_2$  on the combined  $CH_4$  and  $CO_2$  conversion in an APGD plasma, the so-called oxidative  $CO_2$  reforming of methane (OCRM), which allows for stable plasma conditions up to large enough  $CH_4$  fractions, without much soot formation, that can be modelled in a stationary manner, with enough variation in chemical composition, to yield interesting results and obtain the most thorough model validation. These coupled models allow us to obtain otherwise unknown parameters, e.g. temperature and species density profiles, as well as to explain the experimental trends.

The addition of  $O_2$  to  $CH_4$  and  $CO_2$  plasmas would allow for the partial oxidation of  $CH_4$ :

$$CH_4(g) + 0.5O_2(g) \rightarrow CO(g) + 2H_2(g)\Delta H^0 = -36 \ kJ/mol$$

to assist in the conversion of  $CH_4$  besides the dry reforming of  $CH_4$  (DRM):

$$CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g)\Delta H^0 = +247 \ kJ/mol$$

In addition, some other reactions will take place, resulting in (undesired)

side-products (e.g.H<sub>2</sub>O), such as the reverse water–gas-shift and the full oxidation of CH<sub>4</sub>:

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)\Delta H^0 = +41 \text{ kJ/mol}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)\Delta H^0 = -891kJ/mol$$

These reactions would obviously suggest a higher conversion of  $CH_4$  (and  $CO_2$ ) upon addition of  $O_2$ . However, our model indicates that the reality is more complex. Indeed, the large endothermic nature of DRM and the large exothermic nature of the full oxidation of  $CH_4$  greatly affect the temperature in the plasma, which will impact the thermodynamic equilibria and the kinetics of the system. This explains the need for a detailed self-consistent computational model, describing all physics and chemistry in a fully coupled way.

#### 2. Computational and experimental details

#### 2.1. 3D gas fluid dynamics RANS SST model

#### 2.1.1. 3D geometry and equations

Fig. 1 depicts the APGD reactor geometry (left), and the transition to the 3D modelled geometry (middle). We use a tetrahedral mesh, consisting of 18 million elements, including boundary layers, as illustrated in the right picture of Fig. 1.

Understanding the 3D gas flow profile is essential before exploring the 2D axisymmetric model. Indeed, the inlet of the coupled 2D axisymmetric model should not have a negative mass flow at any point. To avoid this, we first studied the inlet flow profile with a 3D fluid dynamics model, describing only the fluid flow equations.

The 3D fluid dynamics model is solved using COMSOL Multiphysics® 6.0 [21]. We describe the gas flow in the reactor using Menter's Shear Stress Transport (SST) turbulent fluid flow model with weakly compressible flow. Specifically, in 3D, we solve these Reynolds-averaged Navier-Stokes (RANS) equations: [22,23]

$$\nabla \bullet (\rho \boldsymbol{u}) = \boldsymbol{0} \tag{1}$$

$$\rho(\boldsymbol{u} \bullet \nabla)\boldsymbol{u} = \nabla \bullet \left[ -p\boldsymbol{I} + (\boldsymbol{\mu} + \boldsymbol{\mu}_T) \left( \nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T \right) - \frac{2}{3} (\boldsymbol{\mu} + \boldsymbol{\mu}_T) (\nabla \bullet \boldsymbol{u}) \boldsymbol{I} - \frac{2}{3} \rho \boldsymbol{k} \boldsymbol{I} \right]$$
(2)

In these equations  $\rho$  is the gas density calculated by the thermodynamic model (see section 2.2 below),  $\boldsymbol{u}$  is the gas flow velocity vector, p is the gas pressure,  $\boldsymbol{I}$  is the unity tensor,  $\mu$  is the dynamic viscosity,  $\mu_T$  is the turbulent dynamic viscosity, k is the turbulent kinetic energy, and superscript T describes transposition.

#### 2.1.2. 2D inlet gas velocity profile

The velocity profile in the APGD results from the flow profile in the groove of the cathode pin. As just the tip of the cathode is considered in the 2D model and the extended groove is omitted, the 2D inlet velocity profile should resemble the flow profile at the corresponding position in the 3D model. The left side of Fig. 2 shows the zx-projection of the 3D model, with a red line indicating the position at which the velocity profiles are transferred to the 2D axisymmetric model. The right side shows the cut plane at this position, to obtain the velocity in cylindrical coordinates as a function of the radius. We take the average velocity value in three cylindrical coordinates (r,  $\varphi$ , z) of 130 circles with radii ranging from 1.85 mm to 2.5 mm, to obtain the 2D axisymmetric inlet velocity profile.

We translate the Cartesian velocity components (of the 3D model) to cylindrical components using the following equations, obtained from the derivation of Cartesian coordinates transformation to cylindrical coordinates with respect to time [24].



Fig. 1. Schematic representation of the atmospheric pressure glow discharge (APGD) reactor (left), the corresponding implementation in the 3D model (middle), and the size of the mesh cells (right). The gas flow is indicated in turquoise.



Fig. 2. Translation of a cut plane in the 3D flow model to the inlet boundary condition of the 2D axisymmetric model.

$$v_r = \frac{dr}{dt} = \frac{d}{dt} \left( \sqrt{x^2 + y^2} \right) = \frac{xv_x + yv_y}{\sqrt{x^2 + y^2}}$$
(3)

$$v_{\varphi} = r \frac{d\varphi}{dt} = \sqrt{x^2 + y^2} \frac{d}{dt} \left( \tan^{-1} \left( \frac{y}{x} \right) \right) = \frac{xv_y - yv_x}{\sqrt{x^2 + y^2}}$$
(4)

$$v_z = v_z \tag{5}$$

#### 2.2. 2D axisymmetric model

#### 2.2.1. Equations

2.2.1.1. Transport of species. The direct current (DC) properties of this plasma allow us to solve a stationary set of equations, because the current and voltage do not change over time. Therefore, the equations are not time-dependent (i.e., all time-dependent terms can be neglected) and we reach a stationary solution with this model.

The transport of species is described using the conservation of mass: [25]

$$\nabla \bullet \boldsymbol{j}_i + \rho(\boldsymbol{u} \bullet \nabla) \omega_i = \boldsymbol{R}_i \tag{6}$$

Here,  $j_i$  is the diffusive flux vector of species i,  $\rho$  is the gas density, u is the gas flow velocity vector,  $\omega_i$  is the weight fraction of species i, and  $R_i$  is the total net production rate of species i. The number of species included in this model is 21, and is determined from the reduction of the chemistry set in the 0D model, as explained in section 2.4 below.

 $j_i$  is obtained from the Maxwell-Stefan diffusion model: [25–27]

$$\boldsymbol{j}_{i} = -\left(\rho D_{i}^{m} \nabla \omega_{i} + \rho \omega_{i} D_{i}^{m} \frac{\nabla M_{n}}{M_{n}} - \boldsymbol{j}_{c,i} + \boldsymbol{j}_{T,i}\right)$$
(7)

Here,  $D_i^m$  is the diffusion coefficient for species *i*,  $M_n$  is the mean molar mass,  $\mathbf{j}_{c,i}$  is the multi-component diffusive flux correction term, and  $\mathbf{j}_{T,i}$  is the turbulent diffusive flux vector.

 $D_i^m$ ,  $M_n$ ,  $j_{c,i}$  and  $j_{T,i}$  are calculated via: [25–27]

$$D_i^m = \frac{1 - \omega_i}{\sum_{k \neq i D_{lk}}}, \ M_n = \left(\sum_i \frac{\omega_i}{M_i}\right)^{-1}, \ \boldsymbol{j}_{c,i} = \rho \omega_i \sum_k \frac{M_i}{M_n} D_k^m \nabla \boldsymbol{x}_k$$
(8)

$$\boldsymbol{j}_{T,i} = \rho \omega_i \boldsymbol{D}_{T,i} \nabla \omega_i, \ \boldsymbol{D}_{T,i} = \frac{\nu_T}{\boldsymbol{S}\boldsymbol{c}_T}$$
(9)

Here,  $x_k$  is the mole fraction of species i,  $D_{i,k}$  is the multicomponent Maxwell-Stefan diffusivity,  $M_i$  is the molar mass of species i,  $D_{T,i}$  is the turbulent diffusivity coefficient of species i,  $\nu_T$  is the turbulent kinematic viscosity and  $Sc_T$  is the turbulent Schmidt number.

2.2.1.2. RANS SST equations. The RANS SST equations are once again solved for a weakly compressible flow, as discussed in section 2.1 (see Eqs. (1) and (2).

The governing equations for the turbulent kinetic energy, k, used in Eq. (2), and the specific dissipation rate,  $\omega$ , are given by: [23,28,29]

$$\rho(\boldsymbol{u} \bullet \nabla)\boldsymbol{k} = \nabla \bullet \left[ (\boldsymbol{\mu} + \boldsymbol{\mu}_T \sigma_k) \nabla \boldsymbol{k} \right] + \boldsymbol{P} - \beta_0^* \rho \omega \boldsymbol{k}$$
(10)

$$\rho(\boldsymbol{u} \bullet \nabla)\boldsymbol{\omega} = \nabla \bullet \left[ (\boldsymbol{\mu} + \boldsymbol{\mu}_{T} \sigma_{\boldsymbol{\omega}}) \nabla \boldsymbol{\omega} \right] + \frac{\gamma}{\boldsymbol{\mu}_{T}} \rho \boldsymbol{P} - \rho \beta \boldsymbol{\omega}^{2} + 2(1 - f_{\nu 1}) \frac{\sigma_{\boldsymbol{\omega} 2} \rho}{\boldsymbol{\omega}} \nabla \boldsymbol{k}$$
$$\bullet \nabla \boldsymbol{\omega}$$
(11)

Here *P* is the turbulent kinetic energy source term,  $\beta_0^*$  and  $\sigma_{\omega 2}$  are turbulence modelling parameters,  $\gamma$ ,  $\beta$ ,  $\sigma_k$  and  $\sigma_{\omega}$  are turbulence parameters depending on the blending functions  $f_{\nu 1}$  and  $f_{\nu 2}$  described in the SI Section S.6. Further description of the turbulence equations and the turbulence modelling parameters can also be found in the SI Section S.6.

2.2.1.3. Heat balance equation. Additionally, we solve a modified heat

balance equation, which accounts for the transport of species and chemistry, to solve the conservation of energy: [26,27,30,31]

$$\rho C_p \boldsymbol{u} \bullet \nabla T + \nabla \bullet (-(\boldsymbol{k} + \boldsymbol{k}_T) \nabla T) + \sum_i \overline{\overline{M}_i} \boldsymbol{r}_i = \boldsymbol{Q} + \sum_i \boldsymbol{j}_i \bullet \nabla \overline{\overline{M}_i}$$
(12)

The first, second and third term at the left-hand side are the convective term, the conductive term, and the term accounting for the heat released and absorbed by chemical reactions. The first and second term at the right-hand side are the heat source mimicking the plasma, and the enthalpy diffusion. Here,  $\rho$  is the density,  $C_p$  is the heat capacity at constant pressure, u is the velocity vector, T is the temperature, k is the thermal conductivity,  $k_T$  is the turbulent thermal conductivity,  $\overline{H_i}$  is the molar mass of species i,  $r_i$  is the reaction rate of species i, Q is the user-defined heat source, which is the power deposited in the plasma, and  $j_i$  is the diffusive flux vector of species i.

As  $C_p$ , k and  $k_T$  depend on the gas composition, they are calculated as follows:

$$C_p = \sum_i \omega_i \times \frac{C_{p,i}}{M_i} \tag{13}$$

where  $\omega_i$  is the weight fraction of species *i*,  $M_i$  is the molar mass of species *i* and  $C_{p,i}$  refers to the heat capacity taken from the NASA polynomial of species *i*, described in section 2.3.4.

The thermal conductivity of the mixture is described by:

$$k = 0.5 \left( \sum_{i} x_i k_i + \frac{1}{\sum_{i} x_i / k_i} \right)$$
(14)

where  $x_i$  is the molar fraction of species *i*, and  $k_i$  is the thermal conductivity of species *i*, calculated using:

$$k_i = 2.669 \times 10^{-6} \frac{\sqrt{TM_i \times 10^3}}{\sigma_i^2 \Omega_k} \times \frac{1.15C_{p,i} + 0.88R_g}{M_i}$$
(15)

Here,  $\sigma_i$  is the characteristic length of the Lennard-Jones potential, and  $\Omega_k$  is the dimensionless collision integral given by:

$$\Omega_k = \frac{b_1}{(T^*)^{b_2}} + \frac{b_3}{exp(b_4T^*)} + \frac{b_5}{exp(b_6T^*)} + \frac{4.998 \bullet 10^{-40} \mu_{D,i}^4}{k_b^2 T^* \sigma_i^6}, \ T^* = T \frac{\varepsilon_i}{k_b}$$
(16)

In this equation,  $b_x$  are empirical constants,  $\mu_{D,i}$  is the dipole constant of species *i*,  $\varepsilon_i$  is the potential energy minimum value and  $k_b$  is Boltzmann's constant. These values are tabulated data taken from literature [29].

Additionally,  $k_T$  is calculated as follows:

$$k_T = rac{\mu_T C_p}{P r_T}$$

With  $Pr_T$  respresenting the turbulent Prandtl number.

Lastly,  $\mu$  and  $\rho$  also depend on the chemical composition, where the former is calculated using:

$$\mu = \sum_{i=1}^{n} \frac{\mu_i}{1 + \frac{1}{x_i} \sum_{j=1, j \neq i}^{n} x_j \phi_{ij}}, \phi_{ij} = \frac{\left(1 + \left(\mu_i / \mu_j\right)^{0.5} (M_j / M_i)^{0.25}\right)^2}{\left(4 / \sqrt{2}\right) \left(1 + M_i / M_j\right)^{0.5}}$$
(18)

In this formula,  $x_i$  is the molar fraction. The dynamic viscosity of species i,  $\mu_i$ , is calculated similar to  $k_i$  in Eq. (15), using:

$$\mu_i = 2.669 \times 10^{-6} \frac{\sqrt{TM_i \times 10^3}}{\sigma_i^2 \Omega_D}$$
(19)

Here,  $\Omega_D$  is expressed similar to Eq. (16):

$$\Omega_{D} = \frac{b_{1}}{(T^{*})^{b_{2}}} + \frac{b_{3}}{exp(b_{4}T^{*})} + \frac{b_{5}}{exp(b_{6}T^{*})} + \frac{4.998 \times 10^{-40} \mu_{D,i}^{4}}{k_{b}^{2} T^{*} \sigma_{i}^{6}}, T^{*} = T \frac{k_{b}}{\varepsilon_{i}}$$
(20)

 $\rho$  is calculated using the ideal gas law:

$$\rho = \frac{pM_N}{R_g T} \tag{21}$$

Here, *p* is the pressure,  $R_g$  is the gas constant, *T* is the temperature and  $M_N$  is the mean molar mass of the mixture.

#### 2.2.2. Geometry and boundary conditions

Fig. 3 depicts the setup of the axisymmetric 2D model. The postplasma region, as shown in the left of the Figure, is included in the axisymmetric simulation, extending the domain to 89 mm in the z direction. An inlet velocity field is defined, as obtained from the 3D model, described in section 2.1.2. The outlet at the end suppresses backflow, while all walls have a no slip condition. A heat source is defined above the cathode pin, following the shape measured by Trenchev et al. [32] Two different heat transfer coefficients, *h*, are defined for the different materials at the walls: glass and ceramic walls are described with  $h = 5W/(m^2K)$  (indicated in purple in Fig. 3), while  $h = 25W/(m^2K)$  is used for stainless steel (both cathode pin and anode plate; indicated in green) [33].

The heat source is described using a Gaussian profile in the r direction and a rectangular profile in the z direction, as shown in Fig. 4. This heat source provides a set power to the model, dependent on the area under the function curves, and this value is multiplied by a constant to reach the desired input power. The shape of the heat source, measured by Trenchev et al. [32], is determined for a  $CO_2$  plasma and not a  $CO_2/$  $CH_4/O_2$  plasma, hence there might be a small difference in the radial profile of the plasma. In this paper we decided to not change the radial profile of the plasma to better fit the experimental results, as this would give the unfair impression that our model is capable of predicting the exact conversion, albeit by fitting the shape of the heat source, which might be unphysical. We rather prefer to claim that we can predict the experimental trends between conditions, with a pure physical model, without any fitting parameter, and gain insights from results which have experimental justification.

The boundary conditions for the SST RANS equations (i.e., Eqs. (1)



**Fig. 3.** Picture of the APGD (left), with detail of the schematic plasma reactor and plasma afterglow image (middle) and translation to the axisymmetric 2D model (right). Boundaries marked on the 2D scheme include: outlet, inlet, two heat transfer coefficients (one for anode steel and one for ceramics and glass) and the heat source.

(17)



Fig. 4. Description of the heat source, using a Gauss function radially and a smoothed rectangle axially.

and (2) in section 2.1.1, and Eqs. (10) and (11) in section 2.2.1.2) are listed in Table 1. <sup>23</sup> $\mu_0$  is the inlet velocity field,  $\boldsymbol{u}|_{l_w=0}$  is the velocity at the wall,  $\hat{p}_0$  is the outlet pressure,  $I_T$  is the turbulent intensity,  $U_{ref}$  is the reference velocity magnitude,  $L_T$  is the turbulent length scale,  $\beta_0^*$  is 0.09, a turbulence model parameter,  $\omega_{visc}^2$  and  $\omega_{log}^2$  are the specific dissipation values for the linear sublayer and logarithmic layers, respectively,  $\boldsymbol{n}$  is the normal vector to the boundary plane,  $h_{\perp}$  is the reference length and  $l_w$  is the closest wall distance.

#### 2.3. 0D chemical kinetics model

#### 2.3.1. Equations

We describe the detailed OCRM plasma chemistry, involving various species related to  $CO_2$ ,  $CH_4$  and  $O_2$  (see Table 4), using ZDPlasKin (Zero-Dimensional Plasma Kinetics solver), which is a Fortran 90 module [34]. This is a 0D model, which calculates the densities of species over time in a non-thermal, uniform plasma with a complex chemistry set.

The OCRM chemistry in the APGD plasma under study is assumed to be thermally driven, due to the high gas temperature (1500–3000 K or above; see Fig. 11 below), meaning that electron impact reactions can be omitted. Furthermore, since electron impact reactions are removed, no power density is defined as input in this model. Instead, the plasma (gas) temperature profile is taken as an input parameter, obtained from the decoupled 2D axisymmetric model, solving only the RANS SST equations and heat balance equation (see section 2.2 above).

The rate of change in density of species *s* depends on its production and loss rates:

$$\frac{dn_s}{dt} = \sum_r \left\{ \left( a_{sr}^R - a_{sr}^L \right) \times k_r \times \prod_l n_l^L \right\}$$
(22)

#### Table 1

Boundary conditions for the SST RANS (flow) equations (Eq. (1), 2, 10 and 11).



The boundary conditions for the heat balance equation (Eq. (12) above, in section 2.2.1.3) are listed in Table 2.) [30] Here  $T_{ustr}$  is upstream temperature,  $\Delta H$  is the sensible enthalpy, q is the heat flux,  $q_0$  is the inward heat flux,  $T_{ext}$  is the external temperature and  $Q_0$  is the user defined heat source.

#### Table 2

Boundary conditions for the heat balance equation (Eq. (12)). The geometry describing the mentioned boundaries is depicted in Table 1.

	T (K)	q (W/m <sup>2</sup> )	Q (W/ m <sup>3</sup> )
Inlet BC	$T_{ustr} =$ 293.15	$-\boldsymbol{n} \bullet \boldsymbol{q} = \rho \Delta H \boldsymbol{u} \bullet \boldsymbol{n} \Delta H = \int_{T_{ustr}}^{T} C_p dT$	/
Walls  CD & EF	/	$-\boldsymbol{n} \bullet \boldsymbol{q} = q_0 q_0 = h(T_{ext} - T)T_{ext} = 293.15Kh = 5W/m^2K$	/
Walls  AB & DE	/	$-\boldsymbol{n} \bullet \boldsymbol{q} = q_0 q_0 = h(T_{ext} - T)T_{ext} = 293.15Kh = 25W/m^2K$	/
Outlet  FG	/	$-\boldsymbol{n} \bullet \boldsymbol{q} = 0$	/
Domain	1	/	$Q=Q_0$

The boundary conditions for the transport of species equation (Eq. (6) in section 2.2.1.1) are listed in Table 3.) [25] Here  $\omega_{0,i}$  is the user-defined inlet mass fraction,  $j_i$  is the diffusive flux vector of species *i* and  $D_i^m$  is the mixture-averaged diffusion coefficient.

Table 3

Boundary conditions for the transport of species equation (Eq. (6)). The geometry describing the mentioned boundaries is depicted in Table 1.

	ω <sub>i</sub> (-)	$J_i (mol/(m^2s))$
Inlet BC	$\omega_i = \omega_{0,i}$	/
Walls AB & CF	/	$-\boldsymbol{n} \bullet \boldsymbol{j}_i = 0$
Outlet  FG	$-\boldsymbol{n} \bullet  ho D_i^m  abla \omega_i = 0$	/

#### Table 4

Species included in the full thermal 0D chemical kinetics model.

Neutral molecules	Radicals
C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> , C <sub>2</sub> H <sub>3</sub> , C <sub>2</sub> H
CH <sub>4</sub>	CH <sub>3</sub> , CH <sub>2</sub> , CH, C
H <sub>2</sub>	Н
CO <sub>2</sub>	
CO	
O <sub>2</sub> , O <sub>3</sub>	0
CH <sub>2</sub> O, HCOOH, CH <sub>2</sub> CO, CH <sub>3</sub> OH,	CHO, COOH, CH <sub>2</sub> OH, CH <sub>3</sub> O, CH <sub>3</sub> CO,
CH <sub>3</sub> CHO, CH <sub>3</sub> COOH, CH <sub>3</sub> OCH <sub>3</sub> ,	CH <sub>2</sub> CH <sub>2</sub> OH, CH <sub>3</sub> CH <sub>2</sub> O, CH <sub>3</sub> CHOH,
CH <sub>3</sub> CH <sub>2</sub> OH, CH <sub>3</sub> OOH	CH <sub>3</sub> OO, HCCO
H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub>	HO <sub>2</sub> , OH

Here,  $n_s$  is the density of species s in m<sup>-3</sup>,  $a_{sr}^R$  and  $a_{sr}^L$  are stoichiometric coefficients of species s at the right and left side of reaction r, respectively. $k_r$  is the reaction rate coefficient of reaction r and  $n_l^L$  is the density of species l on the left side of the reaction.

For a reaction r, we define  $k_r \times \prod_l n_l^L$  as the reaction rate. Multiplying the latter with the stoichiometric coefficients thus results in the production and destruction rates for each reaction.

Reactions r can be described as:

$$a_A A + a_B B(+\delta H) \xrightarrow{\kappa_r} a_C C + a_D D(+\delta H)$$
(23)

Species *A*, *B*, *C* and *D* have  $a_A$ ,  $a_B$ ,  $a_C$  and  $a_D$  as their stoichiometric coefficients, with  $\delta H$  representing the reaction enthalpy in J. The reaction rate coefficients  $k_r$  are derived from the NIST database as an Arrhenius equation, which is a function of temperature, a constant or as a fall-off curve. They are listed in detail in the Supporting Information (SI), along with the original references where the data are adopted from.

#### 2.3.2. Chemistry set

41 Species are included in the chemistry set, shown in Table 4. We divide these species here into neutral molecules and radicals. As mentioned above, we do not include electrons and ions, due to the thermal chemistry. In addition, we do not explicitly include vibrationally excited levels in this model, because at the plasma conditions under study (i.e., gas temperature calculated to be 1500–3500 K), the vibrational distribution function is in thermal equilibrium with the gas temperature

These species undergo 734 reactions, i.e., 726 two-body collisions and 8 three-body reactions, where the third body can be any neutral species. These reactions and their corresponding rate coefficients, as well as the references where the data is adopted from, are all listed in the SI (Section S.1, Table S.1).

#### 2.3.3. Detailed balancing

Reverse reaction rate coefficients to any (forward) reaction rate are often not available, and therefore we use detailed balancing to calculate the missing reverse reaction rate coefficients,  $k_R$ , for the following reaction:

$$aA + bB \xrightarrow{k_F} cC + dD \tag{24}$$

with  $k_F$  the forward reaction rate coefficient. We use:

$$\frac{k_F}{k_R} = e^{\left(\frac{\Delta S^\circ(T)}{R} - \frac{\Delta H^\circ(T)}{RT}\right)} \bullet \left(\frac{1bar}{RT}\right)^{(c+d-a-b)}$$
(25)

With  $\Delta S^{\circ}(T)$  the entropy change of the reaction and  $\Delta H^{\circ}(T)$  the reaction enthalpy, both as a function of the temperature at 1 bar, and *R* the universal gas constant: 8.314 J/(Kmol).

#### 2.3.4. Temperature-dependent $\Delta S$ and $\Delta H$

 $\Delta S$  and  $\Delta H$  are calculated from the change in molar entropy,  $S^{\circ}(T)$ ,

and molar enthalpy,  $H^{\circ}(T)$ , respectively, of species in a reaction. The molar enthalpy and entropy are defined using the 9-term NASA polynomial [35], and additional 9-term polynomials are taken from the work of Burcat [36]. The  $H^{\circ}(T)$  and  $S^{\circ}(T)$  polynomials are both obtained from the  $C_{p}^{\circ}(T)$  polynomial, by integrating  $C_{p}^{\circ}(T)$  and  $C_{p}^{\circ}(T)/T$  with respect to T, respectively:

$$C_{p}^{\circ}(T) = R\left(a_{1}T^{-2} + \frac{a_{2}}{T} + a_{3} + a_{4}T + a_{5}T^{2} + a_{6}T^{3} + a_{7}T^{4}\right)$$
(26)

$$H^{\circ}(T) = RT\left(-a_{1}T^{-2} + a_{2}\frac{\ln T}{T} + a_{3} + a_{4}\frac{T}{2} + a_{5}\frac{T^{2}}{3} + a_{6}\frac{T^{3}}{4} + a_{7}\frac{T^{4}}{5} + \frac{b_{1}}{T}\right)$$
(27)

$$S^{\circ}(T) = R\left(-a_1\frac{T^{-2}}{2} - \frac{a_2}{T} + a_3\ln T + a_4T + a_5\frac{T^2}{2} + a_6\frac{T^3}{3} + a_7\frac{T^4}{4} + b_2\right)$$
(28)

Here,  $^{\circ}$  refers to the standard state of an ideal gas at 1 bar.

 $\Delta S^{\circ}(\mathrm{T})$  and  $\Delta H^{\circ}(T)$  for the example reaction (33) above are therefore:

$$\Delta S^{\circ}(T) = cS^{\circ}_{C}(T) + dS^{\circ}_{D}(T) - aS^{\circ}_{A}(T) - bS^{\circ}_{B}(T)$$
<sup>(29)</sup>

$$\Delta H^{\circ}(T) = cH^{\circ}_{C}(T) + dH^{\circ}_{D}(T) - aH^{\circ}_{A}(T) - bH^{\circ}_{B}(T)$$
(30)

#### 2.4. Reduction of the chemistry set

The full chemistry set above is easily solved by a global/0D model. However, computational costs increase dramatically once this is applied in a multi-dimensional simulation, combined with RANS SST, heat balance and transport of species equations. Therefore, we conducted a sensitivity analysis on the full chemistry set, to reduce the set, by removing species and reactions that are "negligible" (for its criterion: see further) at the conditions under study, similar to the analysis done by Stagni et al. [37].

This sensitivity analysis evaluates how the modeling input, i.e. the species and reactions included in the model, affects the output, and thus, how we can reduce our chemistry set (both species and reactions) within a maximum allowed deviation.

We carried out several 0D simulations for different temperature profiles (all within the expected temperature range for OCRM in the APGD, i.e., 300–4000 K). Note that the actual temperature range is 2000–3500 K, but we took a broader range, for safety. We defined a 'deviation' quantity as the maximum deviation of the reduced set with respect to the total chemistry set, at any point in the simulation.

Specifically, we defined a maximum deviation factor of 0.01, which means that when the calculated molar fraction,  $x_{reduced}$ , of any species of a reduced set at any point during the simulation is greater or smaller than  $x_{full} \pm 0.01$ , the reduced set is considered as invalid. This in turn allows for the removal of species with  $x \le 0.01$ , as long as they are not an important intermediate species for any other species with  $x \ge 0.01$ .

Fig. 5 describes the sensitivity reduction algorithm used to reduce our thermal chemistry set for multi-dimensional modelling. The same principle was applied to the reaction sensitivity analysis. First, every species was attempted to be removed and a deviation was calculated for each species accordingly. Second, the species were ranked with respect to increasing deviation. Simulations were carried out with multiple species deleted. Specifically, for the 41 species, 41 simulations were conducted. The first simulation removed the species with the smallest deviation (T in Fig. 5), the second simulation removed two species with the two smallest deviations (R and T in Fig. 5), the third removed three species, etc. We then calculated the deviations for these corresponding groups of species, and we removed those species belonging to the group with the largest acceptable deviation (R and T, with deviation t in Fig. 5). We applied this procedure for every condition under study

Species   Deviation
Analysis on every speciesSpeciesDeviation QQ1unknown R1Q1unknown R1XS1 </td
Sort $w < x < y < z$ Regroup sortedSpeciesDeviation TRIXQIYX
Analyse groups Species Deviation Species Deviation
Select group with largest acceptableT I 

**Fig. 5.** Sensitivity reduction algorithm used to reduce the thermal chemistry set for multi-dimensional modelling. For every species, we calculate the deviation between the reduced set and the full set. We then sort them from smallest to largest deviation, and combine them in groups, for which we again calculate the deviation. Finally, we select the group with the largest acceptable deviation (in this case: t), and we remove all species belonging to that group. We apply this procedure for each condition (as indicated here by "Temperature profile"). We finally remove the (group of) species that exhibit the largest acceptable deviation for all conditions.

(indicated by Temperature profile in Fig. 5), and finally removed those species from the model that exhibit the largest acceptable deviation for each of the conditions.

After the removal of the least important species, we applied the same steps for the possible removal of the remaining 553 reactions (i.e., which remained after removing of these species). We again carried out one simulation for each omitted reaction. The deviation was calculated for each simulation, ranking them from smallest to largest as we get to the last step. Again we performed 533 simulations: in the first simulation, we removed the reaction with the smallest deviation; in the second simulation, we removed two reactions with the two smallest deviation, etc.

Our final, reduced chemistry set contains 21 species and 57 reversible reactions, as listed in Table 5 and 6, respectively. This chemistry set

Table 5 Reduced set of species, used in the fully coupled 2D axisymmetric model.

Neutral molecules	Radicals
C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> , C <sub>2</sub> H
CH <sub>4</sub>	CH <sub>3</sub>
H <sub>2</sub>	Н
CO <sub>2</sub>	
CO	
O <sub>2</sub>	0
CH <sub>2</sub> O, CH <sub>2</sub> CO	CHO, CH <sub>3</sub> O, HCCO
H <sub>2</sub> O	HO <sub>2</sub> , OH

is used in the 2D axisymmetric model (section 2.2).

#### 2.5. Combined modelling network

The combination of the above models, i.e., the 3D gas flow model, providing input velocity profiles for the 2D axisymmetric model, which then again calculates the gas flow, but now also coupled with heat balance and species transport models, and with input from the 0D model (for the thermodynamic variables and the reduced chemistry set) allows us to obtain a realistic picture of the plasma physics and chemistry, within a reasonable calculation time. The flowchart of the model is shown in Fig. 6. The only input needed is the experimental flow rate, the plasma power and the composition of the inlet mixture.

We start from the 3D RANS SST model, using just the experimental gas flow rate as an input boundary condition. We implement the gas velocity profile obtained in this 3D model (section 2.1.2) as the input boundary condition in the 2D axisymmetric model. We use the full chemistry set (section 2.3.2) to calculate the thermodynamic properties, described in section 2.2.1.3. Using the flow solution, we include the plasma power (implemented as a heat source, as described in section 2.2.2) to solve the heat balance and 2D RANS SST equations. After the reduction of the thermal chemistry set in the 0D model (section 2.4), we implement the reduced chemistry set in the 2D model, and we solve the transport of species (including chemistry) equations (section 2.2.1.1) on top of the results from the heat balance and RANS SST model in the previous step. Note that, in this intermediate step, the heat balance and RANS SST equations are not solved again, but instead we use the

#### Table 6

Reduced set of chemical reactions, used in the fully coupled 2D axisymmetric model. The rate coefficients of all reactions, and the references where the rate coefficients are .

$\begin{array}{l} CH_4 + H \rightleftharpoons CH_3 + H_2 \\ CH_3 + CH_4 \rightleftharpoons C_2H_6 + H \\ CH_3 + CH_3 \rightleftharpoons C_2H_6 \\ C_2H_5 + H_2 \rightleftharpoons C_2H_6 + H \\ C_2H_4 \rightleftharpoons C_2H_2 + H_2 \end{array}$	$\begin{array}{l} CH_3+H\rightleftharpoons CH_4\\ CH_3+CH_4\rightleftharpoons C_2H_5+H_2\\ CH_3+CH_3\rightleftharpoons C_2H_5+H\\ C_2H_2+H\rightleftharpoons C_2H+H_2\\ C_2H+H\rightleftharpoons C_2H+H_2\\ \end{array}$	$\begin{array}{l} C_2H_6+CH_3 \rightleftharpoons C_2H_5+\\ CH_4\\ C_2H_2+CH_3 \rightleftharpoons C_2H+\\ CH_4\\ C_2H_6 \rightleftharpoons C_2H_5+H \end{array}$
$\begin{split} C_2H_4 &\rightleftharpoons C_2H_2 + H_2 \\ \hline CO_2 + H &\rightleftharpoons CO + OH \\ CH_4 + O_2 &\rightleftharpoons CH_3 + HO_2 \\ CH_3 + O_2 &\rightleftharpoons HCHO + \\ OH \\ CH_3 + HO_2 &\rightleftharpoons CH_3O + \\ OH \\ HCO + O_2 &\rightleftharpoons CO + HO_2 \\ C_2H_4 + OH &\rightleftharpoons CH_3 + \\ HCHO \\ C_2H_4 + O &\rightleftharpoons CH_2CO + \\ H_2 \\ HCCO + O &\rightleftharpoons CO + CO \\ + H \\ M + HCHO &\rightleftharpoons M + CO \\ + H_2 \\ HCO + OH &\rightleftharpoons CO + H_2O \\ CH_2CO + OH &\rightleftharpoons CO + H_2O \\ CH_2CO + OH &\rightleftharpoons CH_3 + \\ \end{split}$	$\begin{split} & C_2H + H \rightleftharpoons C_2H_2 \\ & M + CO + H \rightleftharpoons M + HCO \\ & CH_3 + O \rightleftharpoons H + HCHO \\ & CH_3 + O_2 \rightleftharpoons CH_3O + O \\ & H + HCO \rightleftharpoons CO + H_2 \\ & CH_3 + HCO \rightleftharpoons CH_4 + CO \\ & C_2H_2 + OH \rightleftharpoons CH_2CO + H \\ & C_2H_2 + O \rightleftharpoons H + HCCO \\ & CH_2CO + CH_3 \rightleftharpoons C_2H_5 + \\ & CO \\ & H + HCHO \rightleftharpoons CH_3O \\ & HCO + HCO \rightleftharpoons CO + \\ & HCHO \\ & CH_2CO + CH_3 \rightleftharpoons CH_4 + \\ & HCCO \end{split}$	$\begin{split} & C_2H_6 \rightleftharpoons C_2H_5 + H \\ & C_2H_5 \rightleftharpoons C_2H_4 + H \\ & M + CO_2 \rightleftharpoons M + CO + O \\ & M + H + O_2 \rightleftharpoons M + HO_2 \\ & CH_4 + O \rightleftharpoons CH_3 + OH \\ & CH_3 + O \rightleftharpoons CO + H_2 + H \\ & CH_4 + OH \rightleftharpoons CH_3 + H_2O \\ & HCHO + OH \rightleftharpoons H_2O + \\ & HCO \\ & CH_3 + HCHO \rightleftharpoons CH_4 + \\ & HCO \\ & CH_3 + HCHO \rightleftharpoons CH_4 + HCO \\ & CH_2CO + H \rightleftharpoons CH_3 + HCO \\ & CH_2CO + H \rightleftharpoons CH_3 + CO \\ & M + HCHO \rightleftharpoons M + H + \\ & HCO \\ & CH_3O + CO \rightleftharpoons CH_3 + \\ & CO_2 \\ & CH_2CO + H \rightleftharpoons H_2 + \\ & HCCO \\ \end{split}$
CO <sub>2</sub>		

adopted from, can be found in the SI (Section S.2, Table S.2)



**Fig. 6.** Flowchart of the coupled 2D axisymmetric model, with input from 0D and 3D models. The components of the 0D model (reduction of the chemistry set and calculation of the thermodynamic variables) are in blue, the 3D component (input velocity profile) in red, and the 2D models are shown in black. Input and output data is shown in a smaller font, while models are depicted in larger font. Full arrows indicate that the previous equations are also included in the next step, while the dashed arrow indicates only using the previous result as a background. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

previous result as input. Finally, we use the resulting transport of species solution and the previous heat balance and RANS SST solution as an initial condition for the coupled model. From now on, the thermody-namic properties influencing the heat balance and RANS SST equations depend on the mass fractions calculated by the transport of species equation (including chemistry), with the formulations given by the equations in section 2.2.1.3.

#### 2.6. Experimental setup and gas composition

We performed experiments to validate our model, specifically for the combined conversion of  $CH_4$  and  $CO_2$ , with  $O_2$  addition (so-called oxidative  $CO_2$  reforming of methane, OCRM) in an APGD plasma.

We used the reactor shown on the left side of Fig. 3; the ceramic piece (also described in section 2.2.2) is made from MACOR. The inflow of gas

is controlled using Bronkhorst® (F-201CV) mass flow controllers, drawing from 99.5 % purity © Air Liquide gas cylinders (CO<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub>). We analysed the resulting gas mixture using an Agilent 990 Micro gas chromatograph ( $\mu$ GC), with H<sub>2</sub>O being separated using a cold trap, to not damage the equipment. Two channels are used: channel 1 uses a molsieve 5A column and Ar as carrier gas; permanent gases (CO, H<sub>2</sub>, and O<sub>2</sub>) are separated and measured on this channel. Channel 2 uses a PoraPLOT U column and He as a carrier gas, separating CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> from each other and from the other gases. Both channels use a CP PoraBOND Q as pre-column.

The setup used for these experiments is similar to the setup investigated by Wanten et al. [38] Power is supplied to the plasma using a current-controlled Technix HV (SR30KV-1.2KW) power supply. We used a 300 k $\Omega$  ballast resistor connected in series with the plasma to stabilize the current going to the discharge. The current during the experiments was kept constant at 25 mA. Due to the changes in conductivity resulting from the different gas mixtures, the voltage between the different input parameters varies slightly, which in turn results in slightly different deposited power for the same current.

The gas compositions at the inlet investigated experimentally are identical to the gas compositions in the model, as shown in Table 7. The experimental data are obtained from three samples of three measurements at each condition.

In all conditions, we applied a total standard total flow rate of 1 L/ min and the same input current of 25 mA, which gave rise to a similar plasma power (varying between 92.5 and 97.3 W).

#### 3. Results and discussion

Essentially we solve three different models, i.e., a 3D gas flow model, a 0D full chemistry model and the fully coupled 2D axisymmetric model, using input from the other models, as discussed in section 2.5. Although these models are closely linked, we will first discuss them separately. Therefore, in the following sections, we will discuss the chemistry reduction, described in section 2.4, as well as the 3D flow model, described in section 2.1, before presenting the results of the fully coupled 2D axisymmetric model and comparing with the experimental results.

#### 3.1. Global model

As mentioned in section 2.4, starting from the full set of 41 species and 734 irreversible reactions, only 21 species and 57 reversible reactions remain. Fig. 7 compares this reduced set to the original, full set, by plotting the species molar fractions as a function of time. For clarity, only the molar fraction of the major species (CO<sub>2</sub>, H<sub>2</sub>O, CO, H<sub>2</sub>, CH<sub>4</sub>, H, OH, O and O<sub>2</sub>) are plotted, the agreement was similar for all other species as well. For comparison, the pre-defined temperature profile for which the calculations were performed is also plotted (black dashed line, right y-axis). This comparison illustrates that the chemistry reduction was successful.

For the reactions, the forward and reverse reactions are paired, to reduce the computational costs in multi-dimensional modelling, while reactions without a reverse reaction in the reduced set are paired with the reverse reaction found in the full set. This increases the number of

#### Table 7

Initial gas composition and plasma power for the experimental conditions to which we applied our model.

Symbol	CO <sub>2</sub> fraction (%)	CH <sub>4</sub> fraction (%)	O <sub>2</sub> fraction (%)	Measured plasma power (W)
α	63	34	3	96.7
β	59	32	9	97.3
γ	55	30	15	92.5
δ	49	36	15	95.0
ε	42.5	42.5	15	93.8



**Fig. 7.** Comparison between the calculated molar fractions of the major species (with fraction above 0.01), calculated with the reduced chemistry set (full lines) and the complete set (dotted lines), as a function of time, for a predefined temperature profile, plotted in black dashed line (right y-axis).

reactions a bit, from 87 irreversible to 57 reversible reactions, or 114 irreversible reactions. The reduced reaction set can be found in section 2.4 (Table 6), while their corresponding reaction rate coefficients can be found in the SI (Section S.2, Table S.2).

The small deviation of the reduced set is due to the strict deviation margin of 0.01 set on the reduction process, as discussed in section 2.4.

For all calculated temperature ranges, only 11 species ever have molar fractions above 0.01, and Fig. 7 even shows only nine species for this temperature profile. However, the set cannot be reduced below 21 species, because the other species act as important intermediates for the product composition. These extra (12) species include HO<sub>2</sub>, five species originating from the reaction of CH<sub>4</sub> and O<sub>2</sub>, i.e. HCHO, CH<sub>3</sub>O, HCO, CH<sub>2</sub>CO, HCCO, and six resulting from the CH<sub>4</sub> chemistry, i.e. C<sub>2</sub>H, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub>. Combined with the nine species in Fig. 7, we get a total of 21 species, as listed in Table 5 above.

#### 3.2. 3D RANS SST flow model

Fig. 8(a) shows the streamlines of the 3D RANS SST flow simulation, while Fig. 8(b)–(d) illustrate the *r*,  $\varphi$  and *z* components of the velocity, as calculated with Eqs. (3)–(5), respectively. As a result of the nearly

tangential gas input, a swirling flow is initiated within the reactor chamber. The swirling flow creates a small pressure gradient, which creates a backflow in the middle of the reactor [39]. Fig. 8(a) and (d) show clear backflow from the open boundary, as seen by the negative  $v_z$ in plot 8(d). As mentioned in section 2.1.1, the mass flow at the inlet cannot be negative at any position of the 2D inlet, as this would mean that any reacted mass can flow back into the inlet and return as the unreacted inlet mixture, because mass is conserved. The cut plane is shown in Fig. 8 with a light purple line, at 12.5 mm height.

The r component of the velocity is small compared to the other components, reaching at maximum 6.1 and -9.0 m/s, both at the inlet, but with overall values between 1.0 and -1.0 m/s after the inlet cut plane. The  $\varphi$  and z components, on the other hand, are much larger, with  $\varphi$  reaching as fast as 47.9 m/s in the cathode groove. Both show only partial axisymmetric flow, as the magnitude of the velocities is the greatest near the single entrance of the swirling groove flowing into the upper reactor volume. Indeed, the *z* velocity reaches 19.1 m/s at a single point over the cut plane, while being only 0.2 m/s at the opposing site on the cut plane. This indicates that the 2D axisymmetric approach is not perfect, due to the single gas inlet. Reactors with multiple gas inlets, or entrance points, into the symmetric reactor volume are better suited for this approach. Unfortunately, calculating complex plasma-chemical systems in 3D is currently computationally unfeasible, and the chemistry really has to be included for realistic simulations, so the axisymmetric model is the only feasible option.

#### 3.3. 2D axisymmetric model

## 3.3.1. Comparison of modelled and experimental conversion and production composition

First, to validate our model, we compare the calculated CO<sub>2</sub> and CH<sub>4</sub> conversions and the product composition, obtained from the coupled model, with the experimental data at exactly the same conditions. The conversion of species *i* in the model,  $\chi_{i,model}$ , and in the experiments,  $\chi_{i,experiment}$ , are calculated via Eqs. (31) and (32), respectively:

$$\chi_{i,model} = \frac{n_{i,influent} - n_{i,effluent}}{n_{i,influent}}$$
(31)

$$\chi_{i,experiment} = \frac{c_{i.influent} - \alpha \times c_{i.effluent}}{c_{i.influent}}$$
(32)

Where  $n_i$  is the molar flow rate of species *i*,  $c_i$  is the concentration of species *i* and  $\alpha$  is the gas expansion factor, as described by Wanten et al. [40] Fig. 9 depicts the CO<sub>2</sub> and CH<sub>4</sub> conversion for all conditions of



**Fig. 8.** Streamlines calculated with the 3D gas flow model, plotting the velocity magnitude and direction in 3D (a), and three cut plane plots, depicting the r,  $\varphi$  and z velocity (b, c, d).

Table 7. The  $O_2$  conversion is shown in Fig. S.16 in Section S.7 of the SI. The calculated conversion is evaluated at the outlet of the simulation (i. e., at 89 mm), as shown on the right side of Fig. 3.

It is clear that the model overestimates both the  $CO_2$  and  $CH_4$  conversion, which indicates that some complexities in the experiments (e.g., flow turbulence, effect of details in the reactor geometry, chemistry, ...) are not yet captured by our model. Furthermore, as mentioned in section 2.2.2, the conversion will deviate, which is probably due to the estimated heat source shape. This heat source was determined before any simulation result was known and has not been changed, to avoid any fitting in this model, as the latter might give the false impression that our model can already predict the absolute conversion at a single condition, while we aim to predict trends with a pure physical model, without any fitting parameter.

When we look at the trends in conversion across the conditions, we see that the modelled CH<sub>4</sub> conversion trend is correctly describing the experimental trend. Indeed, upon rising O<sub>2</sub> fraction in the mixture (condition  $\alpha$ ,  $\beta$  and  $\gamma$ ), we observe an increase in CH<sub>4</sub> conversion, peaking at condition  $\gamma$  (i.e., 15 % O<sub>2</sub>), followed by a drop in CH<sub>4</sub> conversion for conditions  $\delta$  and  $\epsilon$  (same O<sub>2</sub> fraction of 15 %, but rising CH<sub>4</sub> fraction). The lowest CH<sub>4</sub> conversion was found for condition  $\alpha$ , for both the experimental and modelled condition. This is also the case for the CO<sub>2</sub> conversion. However, the trends of the calculated CO<sub>2</sub> conversion does not change significantly between the various conditions, while there is a clear variation in the calculated CO<sub>2</sub> conversion. This discrepancy, but also the correct CH<sub>4</sub> trend and the correct trend of CO<sub>2</sub> conversion between conditions  $\alpha$  and  $\beta$ , can be explained from the calculated plasma species analysis, to be presented in section 3.3.3.

Fig. 10 depicts the composition at the outlet (i.e., at 89 mm), for both the model and the experiment, for all conditions in Table 7.

In line with the trend in the conversion plot, the calculated CO<sub>2</sub> fraction shows a mismatch with the experiments, specifically for the  $\beta$  and  $\gamma$  conditions. Likewise, the trend of CO molar fraction, increasing for both the model and the experiments from the  $\alpha$  to  $\beta$  condition, is not found when moving toward condition  $\gamma$ . The trends found in the calculated H<sub>2</sub>O and H<sub>2</sub> molar fractions, however, align well with the experimental trends H<sub>2</sub>O reaches a maximum at condition  $\gamma$ , both in the model and experiments, while H<sub>2</sub> shows the opposite trend (again in the model and experiments), reaching a minimum for condition  $\gamma$ .

In general, reasonable agreement is reached between model and experiments for both conversion and product composition, at least for the trends, certainly keeping in mind the complexity of the model and also the experiments (including the chemistry), and that not any fitting



**Fig. 9.** Calculated and experimental  $CO_2$  and  $CH_4$  conversions, for all conditions of Table 7. The calculated conversion is evaluated at the outlet of the simulation (at 89 mm), as shown on the right side of Fig. 3. The error bars in the experimental data are obtained from three repetitions of three measurements at each condition with great reproducibility.



**Fig. 10.** Calculated and experimental molar compositions, for all conditions of Table 7. The calculated molar composition is evaluated at the outlet of the simulation (89 mm), as shown on the right side of Fig. 3.

was used in our model. A setup which would allow more optical diagnostics; could give way a more complete validation of the model by measuring the densities and evolution of transient species. For instance, the measurement of the absolute density of the hydrogen atom in the ground state using TALIF, like done by Huang et al. [41] This will be considered in future work.

The conversion trends also align with thermodynamical expectations, keeping in mind the overall reactions mentioned in the Introduction. However, increasing the CH<sub>4</sub> fraction in conditions  $\delta$  and even further in  $\epsilon$  would thermodynamically favour the full oxidation of CH<sub>4</sub>, resulting in more CO<sub>2</sub> and H<sub>2</sub>O formation. This is not the case, as can be seen in both the model and the experiment. This means that the reality is more complex than simple thermodynamic expectations, and we can use our detailed model to explain the experimental trends. For this purpose, we look at the simplest explanation first, being a change in temperature.

3.3.2. Calculated temperatures and thermodynamic analysis

Fig. 11 depicts the spatial temperature profiles for all conditions of Table 7. The maximum calculated temperature is written for every condition, and is located near the anode plate (z = 25 mm), as most reactions have taken place before this point.



Fig. 11. Axisymmetric 2D temperature profiles for all conditions of Table 7.

Unfortunately, we could not measure the plasma temperature in our APGD reactor. Indeed, we could not use a thermocouple, as it would melt. We performed some tests with a thermocouple, a few millimetres after the plasma, reaching already 1000 K, but closer to the plasma, or inside the plasma, was not possible. Likewise, we could not apply OES because our APGD reactor is made of ceramic. However, a previous study by Deng et al. [42] has shown that the temperature in an atmospheric pressure direct current plasma in the glow regime is around 3000 K for dry air. While the temperature will be somewhat different due to the different gas mixture and slightly different operating conditions, this data shows that our calculated temperatures are in the correct order of magnitude.

The increase in CH<sub>4</sub> conversion upon rising O<sub>2</sub> fraction in the mixture (Fig. 9) can directly be linked to an increase in temperature going from condition  $\alpha$  to  $\gamma$ , as the maximum temperature rises from 2981 K to 3470 K. The decrease in CH<sub>4</sub> conversion upon higher CH<sub>4</sub> fraction in the mixture (also Fig. 9) also coincides with a drop in temperature from condition  $\gamma$  to  $\varepsilon$  (as the maximum temperature drops from 3470 K to 3019 K). Hence, it demonstrates that the CH<sub>4</sub> conversion is indeed dictated by thermal chemistry.

We would expect these trends to be the same for the CO<sub>2</sub> conversion, but it was not the case (Fig. 9). Therefore, we will have to plot the species density profiles, to understand the lower CO<sub>2</sub> conversion at condition  $\gamma$  (see section 3.3.3 below). Furthermore, we need to understand why the temperature profiles follow the above trends, with a rise upon increasing O<sub>2</sub> fraction in the mixture, and a drop upon rising CH<sub>4</sub> fraction. This in turn is directly linked to the enthalpy profiles, which we will discuss first.

Fig. 12 illustrates the enthalpy profiles for all conditions, obtained from the integration of the total heat capacity (Eq. (13) with respect to T, similar to the enthalpy calculation in section 2.3.4.

First, the enthalpies at the inlet for low O2 and rather low CH4 conditions ( $\alpha$  and  $\beta$ , i.e., -7978 kJ/kg and -7509 kJ/kg) are lower (i.e., more negative) than for the higher  $CH_4$  and higher  $O_2$  conditions ( $\gamma,\,\delta$ and  $\varepsilon$ , i.e., -7056 kJ/kg, -6809 kJ/kg and -6535 kJ/kg). This is expected, due to the small molar enthalpy of CO2 at 293 K (-393.5 kJ/ mol). The difference between the maximum enthalpy and the enthalpy at the inlet directly affects the maximum temperature, with a smaller difference yielding a higher maximum temperature (cf. Eq. (12) above). Thus, the lower (=more negative) maximum enthalpy of condition  $\gamma$ (-713 kJ/kg) with respect to conditions  $\alpha$  (-339 kJ/kg) and  $\beta$  (-309 kJ/kg)kJ/kg) explains the increase in temperature at condition  $\gamma$  (see Fig. 11), despite a somewhat lower plasma power (cf. Table 7). Likewise, the less negative enthalpy in condition  $\delta$  (from a maximum of -713 kJ/kg at condition  $\gamma$ , to a maximum of -93 kJ/kg) explains the lower temperature shown in Fig. 11. This trend continues and is even more striking for condition  $\varepsilon$  (highest CH<sub>4</sub> and O<sub>2</sub> fraction and lowest CO<sub>2</sub> fraction), where the maximum enthalpy is positive (+284 kJ/kg), and the



Fig. 12. Total enthalpy profiles of all conditions of Table 7.

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temperature is clearly lower (Fig. 11).

The total enthalpy is temperature and species dependent. Therefore, to fully understand the change in enthalpy, and by extent the change in temperature, we need to obtain a better understanding of the species composition in the bulk and afterglow of the plasma.

#### 3.3.3. Plasma species analysis

Fig. 13 depicts the molar fraction profiles of the dominant eight species (CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, CO, H<sub>2</sub>O, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and HCHO) at conditions  $\alpha$ ,  $\beta$ , and  $\gamma$ .

The CO<sub>2</sub> and CH<sub>4</sub> plots show that these molecules are destroyed closer to the inlet already, at a higher O<sub>2</sub> fraction (i.e., condition  $\beta$  with respect to  $\alpha$ , and condition  $\gamma$  with respect to  $\beta$ ). This can be understood as a direct effect of the higher temperature plotted in Fig. 11. It also explains the higher CH<sub>4</sub> conversion, as shown in Fig. 9.

All the CH<sub>4</sub> is converted in the centre of the plasma (see dark blue colour in Fig. 13), but not necessarily at the walls. This is one of the reasons why the overall measured conversion is not 100 % (see Fig. 9); note that the reason is not due to backreactions in the afterglow, as follows from the afterglow analysis (see section 3.3.5 below). The hotter the plasma, the larger is also the temperature close to the walls/anode ring (see Fig. 11), giving rise to more conversion there as well. At condition  $\alpha$ , not all CH<sub>4</sub> is converted at the walls (see Fig. 13), while more is converted at condition  $\beta$ , and virtually all is converted at condition  $\gamma$ . Indeed, the molar flow rates of CH<sub>4</sub> at the end of the reactor for conditions  $\alpha$ ,  $\beta$  and  $\gamma$  are 3.87x10<sup>-5</sup> mol/s, 7.23x10<sup>-6</sup> mol/s and 7.63x10<sup>-7</sup> mol/s, respectively.

In the high temperature plasma core, the gas mixture mainly consists of the products CO, H<sub>2</sub>, H<sub>2</sub>O, and unreacted CO<sub>2</sub>. The molar fractions of CO and  $H_2$  both drop with increasing  $O_2$  fraction, with CO reaching a maximum of 0.67 at condition  $\alpha$ , and 0.54 at condition  $\gamma$ , and H<sub>2</sub> reaching 0.23 at condition  $\alpha$ , and 0.19 at condition  $\gamma$ . The maximum H<sub>2</sub>O molar fraction increases from 0.16 at condition  $\alpha$ , to 0.27 at condition  $\gamma$ . This shift in gas composition explains the change in the total enthalpy of Fig. 12. Indeed, following Eq. (27), the molar enthalpy of CO, H<sub>2</sub> and H<sub>2</sub>O at 3000 K is -17.0 kJ/mol, 88.7 kJ/mol and -114.2 kJ/mol, respectively. Therefore, we can understand that the higher O<sub>2</sub> fraction in the mixture (and thus lower CO2 and CH4 fractions) shifts the composition from a high molar fraction of CO and H<sub>2</sub> in the plasma to a higher fraction of H<sub>2</sub>O, resulting in the lower (=more negative) enthalpy at condition  $\gamma$ , due to the low molar enthalpy of H<sub>2</sub>O with respect to the molar enthalpies of CO and H<sub>2</sub>. This more negative total enthalpy can explain the higher temperature and thus partly explains the higher CH<sub>4</sub> conversion, at condition  $\gamma$ . To evaluate whether there is also a change in chemistry at high O<sub>2</sub> fractions, we present a chemical analysis on the production and destruction of C<sub>2</sub>H<sub>2</sub> in Fig. 15 below.

It is also clear from Fig. 13 that the destruction of CH<sub>4</sub> at condition  $\gamma$  happens closer to the inlet, compared to the destruction of CO<sub>2</sub>. Indeed, CH<sub>4</sub> and O<sub>2</sub> react together at lower temperatures, allowing for the production of polyatomic radicals and stable species, of which C<sub>2</sub>H<sub>2</sub> and HCHO are the examples plotted. In the case of C<sub>2</sub>H<sub>2</sub>, it is clear that the higher temperature destroys this product due to reaction with oxygenated species. Indeed, the maximum C<sub>2</sub>H<sub>2</sub> molar fraction at condition  $\gamma$  is 0.024, while at condition  $\alpha$  it reaches 0.056. At condition  $\gamma$ , almost all C<sub>2</sub>H<sub>2</sub> is destroyed after the plasma, reducing its molar fraction to 8.2x10<sup>-6</sup>, while the molar fraction at condition  $\alpha$  drops only to 0.027 after the plasma, indicating that either C<sub>2</sub>H<sub>2</sub> is destroyed due to higher temperatures at condition  $\gamma$ , or upon reaction with oxygenated species, like HCHO.

On the other hand, the molar fraction of HCHO increases from  $4x10^{-4}$  at condition  $\alpha$ , to 0.0018 at condition  $\gamma$ . This species is however short-lived, and immediately destroyed again when reaching any higher temperature. Many products of the reaction of CH<sub>4</sub> and O<sub>2</sub>, as mentioned above, behave in the same way as HCHO, having only very short lifetimes (e.g. CH<sub>3</sub>O, CH<sub>2</sub>CO, HCCO, C<sub>2</sub>H<sub>5</sub>, etc.). To know whether the higher HCHO molar fraction or the higher temperature at higher O<sub>2</sub>



Fig. 13. Molar fraction profiles of CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, CO, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and HCHO, for conditions  $\alpha$ ,  $\beta$ , and  $\gamma$ .

content reduces the selectivity of  $C_2H_2$ , we need to look at conditions  $\delta$  and  $\epsilon$ , with lower temperature but equal  $O_2$  fractions.

Fig. 14 depicts the molar fraction profiles of the same eight species (CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, CO, H<sub>2</sub>O, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and HCHO) at conditions  $\gamma$ ,  $\delta$  and  $\varepsilon$ , which allows us to compare the effect of higher CH<sub>4</sub> fraction (and thus lower CO<sub>2</sub> fraction) at constant O<sub>2</sub> fraction.

As shown in Fig. 14, adding CH<sub>4</sub> to the mixture (i.e., from  $\gamma$  to  $\delta$  to  $\varepsilon$ ) results in the reverse trends shown from Fig. 13. The higher CO and especially H<sub>2</sub> molar fractions in the plasma centre lead to a higher enthalpy, explaining the drop in temperature in Fig. 11. Furthermore, more CH<sub>4</sub> in the mixture means a higher molar fraction of C<sub>2</sub>H<sub>2</sub>, reaching a maximum of 0.06 at condition  $\varepsilon$ . However, the molar flow rate at the end of the reactor at condition  $\varepsilon$  is  $2.35 \times 10^{-5}$  mol/s, i.e., very similar to the value at condition  $\alpha$ , i.e.,  $2.22 \times 10^{-5}$  mol/s.

As the maximum temperature is 3019 K for condition  $\varepsilon$ , and 2981 K for condition  $\alpha$ , the C<sub>2</sub>H<sub>2</sub> selectivity largely depends on the temperature. To better understand the effect of temporal species on the plasma behaviour, like C<sub>2</sub>H<sub>2</sub>, which are not the main reaction products, but are produced in the plasma, as well as destroyed, and still resemble a significant portion of the molar composition inside the plasma, we analysed the production and destruction of C<sub>2</sub>H<sub>2</sub>. Specifically, we carried out a full analysis of the effect of C<sub>2</sub>H<sub>2</sub> on the heat balance.

In Fig. 15 the rates of the most important production and destruction reactions of  $C_2H_2$  are plotted for condition  $\alpha$  (a) and  $\gamma$  (b), as a function of radial position, at z = 14 mm.

Fig. 15(a) indicates three important formation reactions: at higher radial distances (around r = 1 mm)  $C_2H_2$  is mostly formed from  $C_2H_4$ , while closer to the center of the plasma, at higher temperatures,  $C_2H_2$  is mainly formed from  $C_2H$ . Furthermore, there is no significant  $C_2H_2$  formation from any oxygenated species. The destruction of  $C_2H_2$  is mostly to  $C_2H$ . The reactions of  $C_2H_2$  with O or OH are less important.

Fig. 15(b) illustrates that the most important production and destruction reactions have not changed from condition  $\alpha$ , but the rates have shifted. The production rates from C<sub>2</sub>H, as well as the destruction rate towards C<sub>2</sub>H, are lower, increasing the relative importance of the other pathways. The production of C<sub>2</sub>H<sub>2</sub> from C<sub>2</sub>H<sub>4</sub> (C<sub>2</sub>H<sub>4</sub>  $\Rightarrow$  C<sub>2</sub>H<sub>2</sub> + H<sub>2</sub>) is now the most important production process, although its maximum reaction rate remains more or less the same as in condition  $\alpha$ . The maximum destruction rate of C<sub>2</sub>H<sub>2</sub> to C<sub>2</sub>H and H (C<sub>2</sub>H<sub>2</sub>  $\Rightarrow$  C<sub>2</sub>H + H), which does not involve any oxygenated species, is reduced from -4660 mol/(m<sup>3</sup>s) in condition  $\alpha$  to -1930 mol/(m<sup>3</sup>s) in condition  $\gamma$ . These changes result in a lower production and destruction rate of C<sub>2</sub>H<sub>2</sub> at condition  $\gamma$ , demonstrating the importance of the temperature profile, and thus also that the change in Fig. 13 for the C<sub>2</sub>H<sub>2</sub> molar fraction is not



Fig. 14. Molar fraction profiles of CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, CO, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and HCHO, for conditions  $\gamma$ ,  $\delta$  and  $\epsilon$ .



**Fig. 15.** Rates of the most important  $C_2H_2$  production and destruction reactions, as a function of the radial distance at z = 14 mm, for condition  $\alpha$  (a) and  $\gamma$  (b). The black dashed line represents the temperature profile (right y-axis).

due to new chemical pathways.

These changes in reaction rates have an impact on the heat balance in the system. Therefore, the heat produced and lost by chemical reactions should be analyzed for conditions  $\alpha$  and  $\gamma$  (see next section). For completeness, the production and destruction rates of C<sub>2</sub>H<sub>2</sub> for the other experimental conditions are plotted in the SI (Section S.3).

#### 3.3.4. Heat balance analysis

Fig. 16 depicts the heat released (or absorbed) by the various reactions for condition  $\alpha$  (a) and  $\gamma$  (b) at z = 14 mm. As these are net rates, the species in bold in each reaction are produced by the net reaction rate. Furthermore, the reactions are written as endothermic; positive values, corresponding to a release of heat, indicate the formation of species at the left side of the reaction, while negative values, indicating a removal of heat, represent the formation of species at the right side of the reaction. Only the most important reactions contributing to heat absorption or release are plotted, and therefore the black line, which represents the total heat absorbed by all reactions, does not exactly match the sum of the separate reaction heats in this figure. Not all reactions could be listed in the plot, for clarity; they are indicated with labels (a-f): a) C<sub>2</sub>H<sub>2</sub> + H  $\approx$  C<sub>2</sub>H + H<sub>2</sub>, b) CH<sub>2</sub>CO + H  $\approx$  CH<sub>3</sub> + CO, c) H + HCHO  $\approx$  CH<sub>3</sub> + O, d) CO<sub>2</sub> + H  $\approx$  CO + OH, e) CO + H<sub>2</sub>  $\approx$  H + HCO, f) CO + H<sub>2</sub>O  $\approx$  HCO + OH.

Fig. 16(a) indicates that for condition  $\alpha$  the most important reaction removing heat via chemistry is the dissociation of C<sub>2</sub>H<sub>2</sub> to C<sub>2</sub>H and H, with a maximum heat removal of  $1.8 \times 10^9$  W/m<sup>3</sup>. This indicates the importance of the C<sub>2</sub>H<sub>x</sub> chemistry on the plasma heat balance.

Fig. 16(b) illustrates the heat released in condition  $\gamma$ . The temperature profile at this conditions was plotted in Fig. 15(b) and should be kept in mind when discussing the major differences. Firstly, the trend shown in Fig. 15 has large implications here as well: the lower production and destruction rates for C<sub>2</sub>H<sub>2</sub> compared to condition  $\alpha$  do not

only have an impact on the molar fraction of  $C_2H_2$  but also on the exchange of heat. The maximum heat absorbed by the reaction of  $C_2H_2$  into  $C_2H$  and H drops to  $8 \times 10^8$  W/m<sup>3</sup>, and this reduces the amount of heat removed at r = 0.8 mm. Moreover, there is even a release of heat upon chemical reactions at r = 1.6 mm (cf. black curve), driven by the same reactions releasing heat in Fig. 16(a). The reduced heat removal via reactions at condition  $\gamma$  allows for a higher temperature to be reached, which is accompanied by several new endothermic reactions (e and f in Fig. 16(b)). As the total heat balance of Eq. (12) still has to be satisfied at each position, the absorbed and released heat at each position has to be compensated by the other heat balance terms, as we will explain below. The heat absorbed by reactions for all other conditions can be found in the SI (Section S.4).

In Fig. 17 we plot the important terms of the heat balance equation as a function of radial distance, at z = 14 mm, for conditions  $\alpha$  (a) and  $\gamma$  (b). The terms of enthalpy diffusion, axial conduction and both radial and axial turbulent conduction are not indicated, due to their low importance. All terms of Eq. (12) are moved to the right side, resulting in a zero sum.

Fig. 17(a) clearly indicates the importance of the terms due to radial conduction (purple) and the heat of reactions (blue) near the center, where the convective heat losses (green and red) are near zero. Note that the heat of reactions term is equal to the (inverted) black line in Fig. 16 (a), which shows the origin of the features in this term. The radial component of the conductive heat loss compensates for these features, keeping the sum of these two terms equal to the heat source Q (orange). As Fig. 15(a) shows no such features in the radial temperature profile at z = 14 mm, these features in the radial thermal conductivity term originate from the thermal conductivity *k*. Essentially this means that *k* cannot be considered constant in any global model describing this chemistry, and has to include the effect of chemical reactions to satisfy a correct heat balance profile. Importantly, this stresses the limitations of



Fig. 16. Heat released (or absorbed, when negative) by the most important reactions, and for the sum of all reactions (black), as a function of the radial distance at z = 14 mm, for condition  $\alpha$  (a) and  $\gamma$  (b). Reactions a-f are: a)  $C_2H_2 + H \Rightarrow C_2H + H_2$ , b)  $CH_2CO + H \Rightarrow CH_3 + CO$ , c)  $H + HCHO \Rightarrow CH_3 + O$ , d)  $CO_2 + H \Rightarrow CO + OH$ , e)  $CO + H_2 \Rightarrow H + HCO$ , f)  $CO + H_2O \Rightarrow HCO + OH$ .



Fig. 17. Most important terms in the heat balance equation (Eq. (12), as a function of the radial distance at z = 14 mm, for condition  $\alpha$  (a) and  $\gamma$  (b).

commonly used global/OD models. Furthermore, near the edges, the radial conduction compensates for the heat losses from both radial and axial convective terms, which again, due to the complexity of the flow field, cannot be considered in a flow-averaged global model.

Fig. 17(b) illustrates the same trends, with a major difference being the effect of *k* at r = 1.6 mm, where exothermic reactions force *k* to displace heat, while for condition  $\alpha$ , at r = 1.6 mm, *k* deposits heat. This demonstrates once again the significant effect of the heat of reactions on the thermal conductivity. The heat balance equation terms for all other conditions can be found in the SI (Section S.5).

To summarize, the heat balance equation shows that the significant features in the thermal conductivity plot, depend on the reaction heat exchange and the user-defined heat source, and subsequently, they influence the temperature profile, determining the gas composition, and by consequence, also the reaction heat exchange. This is an important finding of our model, because it reveals that the thermal conductivity cannot be approximated via linear or quadratic dependencies on the gas temperature. The non-locality of the system, see also section 3.3(f) below, influences the thermal conductivity, as it is coupled to the gas composition via Eq. (15). Hence, it stresses the need of using a fully coupled 2D axisymmetric model.

#### 3.3.5. Afterglow analysis

As the measured conversion and product compositions do not necessarily correspond to the situation right after the plasma reactor, but can be subject to additional chemistry in the plasma afterglow, we can also use our model to obtain more insights in the molar fractions and temperature in the afterglow. Fig. 18 shows the temperature and molar fractions of species (>0.01) in the afterglow, starting after the heat source (z = 30 mm) until the outlet (z = 89 mm), at r = 0 mm. The solid and dashed lines represent conditions  $\alpha$  and  $\gamma$ , hence an O<sub>2</sub> fraction in the mixture of 3 and 15 %, respectively.

First, the trends described earlier are again visible in the beginning of the afterglow. Adding more  $O_2$  (i.e., from condition  $\alpha$  to  $\gamma$ ) results in an increase in H<sub>2</sub>O, the removal of C<sub>2</sub>H<sub>2</sub> and CH<sub>4</sub> and a drop in H<sub>2</sub> molar fraction. Although the CO<sub>2</sub> molar fraction rises as a function of distance in the afterglow at condition  $\alpha$ , this is not due to the recombination of CO into CO<sub>2</sub>. Indeed, due to the presence of H atoms, there is no O<sub>2</sub> present in the afterglow, as the O atoms rather react with H atoms into H<sub>2</sub>O instead of forming O<sub>2</sub>. Therefore, the formation of CO<sub>2</sub> would proceed via the water-gas shift reaction, in which CO and H2O react into H2 and CO<sub>2</sub>. As neither the H<sub>2</sub> nor the H<sub>2</sub>O molar fraction significantly change upon rising distance in the afterglow, we can conclude that the water--gas shift reaction does not occur. Furthermore, for the water-gas shift reaction to occur at this timescale (i.e., a few milliseconds), the gas should be above 2000 K, which it is not the case at condition  $\alpha$ . The change in the molar fraction of CO<sub>2</sub> upon rising distance should thus have another reason. Indeed, looking at Fig. 13 (for condition  $\alpha$ ), we can see that the CO<sub>2</sub> molar fraction at the top clearly varies in the radial direction. This is due to the low CO2 conversion near the walls (similar to



Fig. 18. Temperature and molar fractions of  $CO_2$ ,  $CH_4$ ,  $O_2$ , CO,  $H_2$ ,  $C_2H_2$  and  $H_2O$ , plotted over the afterglow (z = 30 mm to z = 89 mm, for r = 0 mm), for condition  $\alpha$  and  $\gamma$ . 30 mm denotes the beginning of the afterglow.

the CH<sub>4</sub> conversion trend discussed earlier).

In conclusion, our model reveals that the increase in  $CO_2$  and decrease in CO molar fraction as a function of distance in the afterglow (Fig. 18) is not due to the chemistry, but simply due to the mixing of the gas molecules near the walls and in the centre. The same is true for the increase in  $CH_4$  and  $C_2H_2$  molar fractions in the afterglow at condition  $\alpha$ . Species with a molar fraction that is less radially dependent, e.g.  $H_2$  (see Fig. 13), do not exhibit a large variation in molar fraction as a function of distance in the afterglow, which demonstrates there are no significant chemical reactions occurring in the afterglow, as the temperature is too low already.

In contrast to this, the afterglow at condition  $\gamma$  shows some variation in H<sub>2</sub> and H<sub>2</sub>O molar fractions, as well as in the CO and CO<sub>2</sub> fractions. Figs. 13 and 14 demonstrate that this is not due to mixing, as the molar fraction of H<sub>2</sub> is not radius-dependent at the end of the plasma. Instead, the higher H<sub>2</sub>O fraction and lower H<sub>2</sub> fraction at condition  $\gamma$  allow the exothermic water–gas shift reaction to occur in the model. This reaction enhances the H<sub>2</sub> molar fraction from 0.145 to 0.187, and the CO<sub>2</sub> molar fraction from 0.107 to 0.156. Hence, this explains the drop in CO<sub>2</sub> conversion in Fig. 9 for condition  $\gamma$ . As Fig. 9 does not show the same drop in the experimental CO<sub>2</sub> conversion, we may conclude that the afterglow is probably too hot in the model, which gives rise to chemical reaction pathways (such as the water–gas shift reaction) that are not occurring in reality, creating the discrepancy between calculated and measured CO<sub>2</sub> conversion trend towards condition  $\gamma$ .

Fig. 19 illustrates the temperature and molar fractions of species (>0.01) in the afterglow, starting after the heat source (z = 30 mm) until

the outlet (z = 89 mm), with the solid and dashed lines represent condition  $\gamma$  and  $\epsilon$ , hence a low CH<sub>4</sub> and high CO<sub>2</sub> fraction, and a high CH<sub>4</sub> and low CO<sub>2</sub> fraction, respectively, at constant O<sub>2</sub> fraction of 15 %.

A higher CH<sub>4</sub> fraction in the mixture (condition  $\varepsilon$ ) results in a lower H<sub>2</sub>O and higher H<sub>2</sub> molar fraction in the plasma (see Fig. 14). Combined with the lower temperature (see Fig. 11), the water–gas shift reaction does not proceed in the model, in contrast to condition  $\gamma$ . Worth to note is the drop in molar fraction of CO<sub>2</sub>, reaching 0.052 at the outlet for condition  $\varepsilon$ , while it is 0.156 for condition  $\gamma$  and 0.187 for condition  $\alpha$  (cf. Fig. 18). Indeed, at condition  $\gamma$ , the CO<sub>2</sub> molar fraction rises from 0.107 to 0.156 (from z = 30 mm to z = 89 mm), which is much more than the rise in CO<sub>2</sub> molar fraction at condition  $\varepsilon$  (from 0.036 to 0.053). Together with the H<sub>2</sub>O and H<sub>2</sub> trends (i.e., their molar fractions barely change upon rising distance for condition  $\varepsilon$ ), this indicates again that the water–gas shift reaction does not occur in the afterglow at condition  $\varepsilon$ . The small increase in C<sub>2</sub>H<sub>2</sub> and CH<sub>4</sub> fraction at condition  $\varepsilon$  is again due to mixing of the molecules from the centre and the walls, as discussed before.

#### 3.3.6. Importance of diffusion and convective fluxes

Finally, we want to stress the importance of diffusion and convective fluxes in determining the gas composition and temperature, and in general, the reactor performance. In the introduction we mentioned that previously LCE approaches were used in multi-dimensional plasma models [14,15]. The validity of these models depends on the locality of the chemistry, i.e. whether the temperature completely dictates the chemical composition. To understand whether this assumption is valid or not for the conditions under study, we performed additional simulations with no convective fluxes, and small diffusion coefficients of  $1 \times 10^{-4} \text{ m}^2/\text{s}$ , with temperature profiles equal to the temperature profiles in the coupled model. Fig. 20 compares our model, including both fluxes (full model; F), with a model neglecting the convective flux and very limited diffusion (so-called local model; L) for the CO<sub>2</sub>, H<sub>2</sub>, CO and H molar fractions, at condition  $\gamma$ .

There is a clear difference in results between the local model and the full model including the computed fluxes. This shows that the LCE approach, as used in previous models in literature, is not applicable for the conditions under study here, i.e., OCRM in a warm plasma, at the timescale in which the gas typically passes through the APGD (1  $\sim$  3 ms). The chemistry is too slow to reach equilibrium, even in the centre of the plasma; cf. the molar fraction of H, which reaches 0.15 in the local model, while it is negligible in the full model.

As the flow is predominantly described by the axial direction (see







Fig. 20. Molar fractions of CO<sub>2</sub>, H<sub>2</sub>, CO and H, obtained from a local, low flux (L) model and a full model including diffusive and convective fluxes (F), at condition  $\gamma$ .

Fig. 8), radial concentration gradients in the local model (L), which are absent in the full model (F), are due to mostly diffusive fluxes and not convective fluxes. This further stresses the importance of including both correct diffusive and convective fluxes in this model.

To summarize, multi-dimensional models using the LCE approach can be significantly different from models including the correct fluxes, as demonstrated here for OCRM in warm plasma. Indeed, the temperature and chemical composition profiles strongly depend on these fluxes, and therefore, the only correct way to describe this system is a fully coupled model. Therefore, and more in general, the LCE approximation should be considered with caution for all chemistries in warm plasma models. Applying the LCE approximation in this case would overestimate the conversion; and considering endothermic reactions, a model including heat transfer calculations with an LCE approximation would severely underestimate the true plasma temperature.

#### 4. Conclusion

We developed a new, fully coupled multi-dimensional model for plasma-based gas conversion, based on a 2D axisymmetric model (describing the gas flow, heat balance, and species transport and chemistry), in combination with a 3D gas flow model and a 0D detailed plasma chemistry model (which both provide input to the 2D model). The combination of these models helps to understand the chemistry and physics occurring in warm plasmas.

We applied this model to an atmospheric pressure glow discharge plasma in a  $CO_2/CH_4$  mixture with  $O_2$  addition (so-called oxidative  $CO_2$ reforming of  $CH_4$ ; OCRM), and compared the calculated  $CO_2$  and  $CH_4$ conversion and product composition with experiments performed at exactly the same conditions. Specifically, we compared our results at five different conditions, reflecting different inlet gas compositions. Although the absolute values still show some discrepancies (illustrating the complex physical and chemical system, which cannot all be captured yet by our model), we found a reasonable agreement in the trends for the different conditions, certainly keeping in mind that our model did not use any fitting to reach agreement with the experiments. Therefore, the model can be used to explain the observed experimental trends.

Our model predicts the highest gas temperature for the highest  $O_2$  fraction in the mixture (condition  $\gamma$ , as compared to conditions  $\alpha$  and  $\beta$ ), and the temperature drops upon higher CH<sub>4</sub> fractions (conditions  $\delta$  and  $\varepsilon$ ). This can be explained by the higher amount of H<sub>2</sub>O present in the plasma at the highest  $O_2$  fraction, which has a low molar enthalpy compared to CO and H<sub>2</sub>, and results in a lower (=more negative) overall enthalpy for condition  $\gamma$ , resulting in the highest temperature. This higher gas temperature can explain the higher CH<sub>4</sub> conversion upon

rising  $O_2$  fraction in the mixture, as also observed experimentally. In addition, chemical reactions also allow for a lower enthalpy of the resulting gas mixture in the plasma, showing the thermal character of the conversion process.

The calculated CO<sub>2</sub> conversion reaches its minimum at the highest O<sub>2</sub> fraction and lowest CH<sub>4</sub> fraction in the mixture (condition  $\gamma$ ), while the measured CO<sub>2</sub> conversion does not exhibit clear variations among the different conditions tested. The reason for the calculated trend is that our model predicts the occurrence of the water–gas shift reaction in the afterglow (CO + H<sub>2</sub>O → CO<sub>2</sub> + H<sub>2</sub>), because of the higher H<sub>2</sub>O molar fraction at the highest O<sub>2</sub> and lowest CH<sub>4</sub> fraction in the mixture (also observed experimentally). However, the fact that the measured CO<sub>2</sub> conversion does not exhibit the same trend, indicates that this reaction in the afterglow is overestimated in the model, probably due to too slow cooling in the afterglow. Therefore, in future work, we will study how our model can result in faster cooling in the afterglow (probably due to more gas turbulence effects), to better reflect reality.

We also demonstrate that approximations of previous models, i.e. both for global models, which assume a constant or temperaturedependent thermal conductivity, as well as for multi-dimensional models, using a local chemical equilibrium approach, would not be valid at the conditions under study, as these approximations do not reflect the true complexity of the system, hence, stressing the need for a fully coupled 2D axisymmetric model.

In general, our new model can capture the major physics and chemistry, even in complex gas mixtures, such as  $CO_2/CH_4/O_2$ , solely using the plasma power, gas flow rate, gas inlet composition and reactor geometry as input, while all other quantities are self-consistently calculated and not any fitting is used. This indicates an important step towards predictive modelling for plasma-based gas conversion.

#### CRediT authorship contribution statement

Stein Maerivoet: Validation, Methodology, Investigation, Formal analysis, Writing & original draft, Conceptualization. Ivan Tsonev: Validation, Methodology, Investigation, Formal analysis, Writing & original draft, Conceptualization. Joachim Slaets: Methodology, Investigation, Conceptualization. François Reniers: Writing – review & editing, Supervision, Project administration, Funding acquisition. Annemie Bogaerts: Writing – review & editing, Supervision, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Stein Maerivoet reports financial support was provided by Research Foundation Flanders. Stein Maerivoet reports financial support was provided by European Research Council. Annemie Bogaerts reports financial support was provided by European Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2024.152006.

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