Non-oxidative methane conversion using nanosecond pulsed discharges: 2D CFD modelling

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Abstract: The conversion of CH_4 to higher order olefin products is of interest, as oil-based olefin production is expected to decrease. There is scope to develop a better understanding of CH_4 conversion using nanosecond pulsed discharges through the use of computational fluid dynamics (CFD) models coupled to plasma physics. In this work we describe a new CFD model that is utilised to study the streamer to spark discharge in the context of CH_4 conversion, with comparison to 0D models and experiments.

Keywords: Nanosecond pulsed discharge, CFD Simulation, Methane, Olefins, Conversion

1. Introduction

Oil-based products, such as short chain hydrocarbons, are an important feedstock material for many industrial processes. The depletion of oil reserves, as well as global trends towards a reduction in extracted oil, means development of alternative sources for these products is of interest [1]. Any new source for these products should also minimise environmental impacts, therefore there is a need for a process that, ideally, can use 100% electricity from renewable sources.

CH₄ is a candidate as a substitute resource for the production of light olefins, as it can be readily extracted from multiple sources, including non-fossil fuel sources [2][3]. Using a plasma to convert CH₄ into higher order products is one approach that, in principle, may only require electricity. Electricity that could be supplied by renewable sources.

Previous work to investigate CH₄ conversion has utilised Non-Thermal Plasma (NTP) in the form of Nanosecond Pulsed Discharges (NPDs) [4][5]. This previous work has demonstrated that after exposure to NTP conditions, the conversion of CH₄ can be adjusted using control parameters such as pressure and power density fed into the discharge, making it possible to control the conversion ratio of the CH₄ into acetylene (C₂H₂), ethylene (C₂H₄), or ethane (C₂H₆). Through the use of 0D modelling with the ZDPlasKin software, kinetic pathways that lead to the observed product ratios in these NPD plasmas have been identified [6].

In order to further develop and understand the processes that lead to CH₄ conversion, it is of interest to develop predictive models that can capture the physics of the plasma and couple this with the insights from chemical kinetics and experimental studies. In the work that is to be presented, a new 2D axially symmetric model has been constructed which couples the equations governing plasma, heat transfer and fluid dynamics together, to simulate both the formation of a streamer, the transition into a spark discharge and the resulting chemical composition of the afterglow, in a pin-to-pin NPD CH_4/H_2 plasma at atmospheric pressure.

2. Methodology

The COMSOL multiphysics software is utilised in order to carry out 2D modelling of nanosecond pulsed discharges in a pin-to-pin reactor. The simulation domain features a pin-to-pin geometry with an anode to cathode surface area ratio of 1 to 4, as shown in figure 1.



Fig 1. (a) Circuit diagram attached to the cathode and anode of the simulation domain. (b)
Dimensions of the simulation domain, including the anode and cathode radius (R_{ano}, R_{cath} respectively), and mesh resolution.

A reduced version of a chemical kinetics scheme, previously developed [6], is incorporated into the model. It uses 9 charged and 11 neutral species listed in table 1.

Table 1. List of species included in the model

Neutral species	Positive species	Negative species
$\begin{array}{c} CH_4,H_2,H,\\ CH_3,CH_2,\\ CH,C_2H_6,\\ C_2H_5,C_2H_4,\\ C_2H_3,C_2H_2 \end{array}$	$\begin{array}{c} CH_{5}^{+}, CH_{4}^{+}, \\ CH_{3}^{+} C2H_{5}^{+}, \\ H_{3}^{+} H_{2}^{+} H^{+} \end{array}$	e ⁻ , H ⁻

A mass-continuity equation is solved for each nonelectron species and the transport is determined by the drift-diffusion approximation, coupled with Poisson's equation for the charged species:

$$\rho \frac{\partial \omega_k}{\partial t} + \nabla \cdot \mathbf{\Gamma}_k = R_k \tag{1}$$

$$\mathbf{\Gamma}_{\mathbf{k}} = \pm n_k (\mu_k \cdot \mathbf{E}) - D_k \nabla n_k \tag{2}$$

$$\nabla \cdot (\varepsilon_o \varepsilon_r \boldsymbol{E}) = \rho_q \tag{3}$$

Where ρ is the species density, ω_k is the species mass fraction, Γ_k is the mass flux of a given species, R_k is the source rate. For equation (2), n_k is the species density, μ_k is the mobility, **E** is the electric field, and D_k is the diffusion coefficient. For a non-charged species, the electric field term is not used. In equation (3), ε_0 is the permittivity of free space, ε_r is the relative permittivity and ρ_q is the total charge density.

The electron energy transport is solved for under the assumptions of the electron energy conservation equation:

$$\frac{\delta n_{\varepsilon}}{\delta t} + \nabla \cdot \Gamma_{\varepsilon} + \mathbf{E} \cdot \Gamma_{e}$$
$$= S_{en} - (\mathbf{u} \cdot \nabla) n_{\varepsilon} + Q_{e}/q_{e}$$
(4)

where n_{ε} is the electron energy density, Γ_{ε} is the flux of the electron energy, **u** is the velocity of the species in the gas, S_{en} is the energy lost or gained due to inelastic collisions, Q_{ε} is an external heat source supplied to the electrons and q_{e} is the charge of an electron.

Reaction rates determined in the plasma module result in a heating term for the bulk gas via both electron impact reactions and enthalpy changes within the chemistry. The bulk gas temperature is determined using the energy conservation equation as follows:

$$\rho C_p \frac{\delta T}{\delta t} + \rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \boldsymbol{q} = Q$$
(5)

here ρ is the gas density, Cp is the heat capacity of the gas, T is the gas temperature, q is the local heat flux density and Q is power density in the gas.

The Navier-Stokes equation can also be solved using the laminar flow assumption to determine the velocity of the species in the gas phase, but in the currently reported results, this has not been included.

Boundary conditions are applied at the electrodes, including a 300 K fixed electrode temperature. A secondary electron emission coefficient is applied to both electrodes, whilst an electron field emission condition is imposed only on the cathode.

Electron impact reaction rates and the electron mobility have been calculated in terms of the mean electron energy using the BOLSIG+ software, and are used as input into the COMSOL multiphysics environment. Energy loss in the system via vibrational and electronic excitation is not explicitly tracked, but it is incorporated into the reaction set. No radiative terms are included, with a low background electron density applied to the model in order to supply an initial source of electrons to start the streamer cascade process.

3. Results

The chemistry of a streamer and spark discharge is driven by the power given to the system from the circuitry. In the presented model, a single pulse is considered. The voltage and current traces of this pulse were utilised to calculate the power deposited into the gas, as shown in figure 2.



Fig 2: (a) Current and voltage pulse for an applied voltage (V_p) of 25 kV, resulting in a maxima of 12 kV due to the coupled circuit and interaction with the plasma. (b) Instantaneous power deposited into the simulation domain from the circuit, as obtained from the product of current and voltage.

The voltage on the anode rises after 1 ns up to a maxima of 12kV at 2.5 ns. As the voltage rises, the current through the system remains low. This is due to a low

density of free charges in the simulation domain that would allow a current to pass through the gas.

The rising voltage on the anode drives the advance of a streamer head from the electrodes. Once the streamer heads connect, an ionised path is formed and a large current is driven through the plasma. This results in a large amount of power being deposited into the gas, which peaks at approximately 0.75 MW, as shown in figure 2 (b). After this large peak in power, the voltage and current drop from a peak value of 12 kV and 120 A, respectively, and a steady voltage of 1 kV and 10 A is sustained in a spark condition. This results in a power deposition of approximately 14 kW into the plasma for a duration of 8 ns. In total, approximately 2 MW of power is put into the system. Afterwards, the voltage and current, and thus also the deposited power, drop to zero, until the start of the next pulse.



Fig 3. Streamer progression across the simulation domain at a time of 2.23 ns. (a) The electron density is at a maximum on the anode, with an ionised region extending outwards. The same is shown on the cathode (to a lower extent), indicating the double streamer head, propagating from both cathode and anode. (b) The reduced electric field is low within the ionised regions and concentrated on the head of the streamers, and especially also close to the cathode.

The propagation of a streamer can be followed by considering both the formation of an ionised region in the gas and the movement of a local maximum in the reduced electric field. Both of these features are shown in figure 3. The physics of positive streamer propagation for atmospheric gases between two pin electrodes typically results in a double streamer head propagating from both the cathode and anode [7]. This is observed to be the case in this work as well. The large reduced electric field is caused by a charge separation of the ions from the electrons due to a difference in mobility in the presence of an electric field, causing a propagating electric field to move across the simulation domain and the ionisation of the gas. A similar difference in the ion and electron densities causes the formation of a large electric field on the cathode, which is mitigated by the field emission coefficient on the cathode.

Previous work has studied the evolution of the chemistry in this NPD using a 0D chemical kinetics model. A comparison of the neutral species densities after one pulse with a similar power density is made in figure 4. As the 2D model contains spatial information, which is not present in the 0D model, a volume average is taken for the neutral species densities within the 2D simulation domain, to simplify the interpretation and comparison.



Fig 4. Comparison of the species densities calculated with the 0D chemical kinetics model [6] and the 2D model described in this work with reduced chemistry set.
(a) Temporal change of the maximum density of C₂H₆, for one pulse and its afterglow. (b) Neutral species densities calculated after 1 ms.

During the propagation of the streamer, radicals and ions are formed in the ionised region. After the streamer has connected the electrodes, the current that is driven through the gas begins to heat the gas through electron collisions. The formation of radicals and the heating of the gas start to drive chemical reactions in the system, such that after the voltage and current is removed, the production of C_2 species increases (see figure 4(a)). After approximately 0.3 ms, the volume-averaged C_2H_6 density is observed to reach an equilibrium, though spatial variations may exist. After one pulse, the trends in the species densities shown in figure 4(b) show reasonable agreement to the expanded chemistry set used in the 0D model, demonstrating that pathways identified in the 0D model can be extended to the 2D model. Using the 2D model, additional insight can be given into how the plasma evolves as a result of the formation of these spark discharges, and the distribution and flow of the species through a reactor. These results demonstrate the capability of the 2D model that should allow for the investigation of new reactors and the influence of external factors, such as geometry, surface effects and gas composition.

4. Conclusion

We present the development of a 2D axisymmetric CFD model with coupled plasma chemistry and heat transfer equations for a study of CH_4 conversion in a nanosecond pulsed discharge in the context of olefins synthesis. Our simulation results demonstrate good agreement with 0D chemical kinetics studies, and provide additional information on the (double) streamer development between cathode and anode. Further development of this model promises a greater understanding of the role of plasma and the importance of reactor design for the optimisation of CH_4 conversion into olefins.

Acknowledgements

We gratefully acknowledge the financial support by the Flemish Government through the Moonshot cSBO project "Power-to-Olefins" (P2O; HBC.2020.2620).

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