Determination of the dominant reaction pathways governing the oxidation of methane in an atmospheric pressure dielectric barrier discharge.

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Abstract: A one-dimensional fluid model is developed for an atmospheric pressure dielectric barrier discharge at 300 K used as a chemical reactor for gas conversion, in a methane-oxygen and a methane-carbon dioxide gas mixture. The model describes the gas phase chemistry in the discharge gap governing the conversion process of methane to higher oxygenates and syngas. The spatially averaged densities of the various plasma species as a function of time are discussed. Besides, the conversion of the inlet gases and the yields of the reaction products as a function of the residence time in the reactor are presented and validated by experiments carried out for the same reactor setup and operating conditions. Furthermore, the main underlying reaction pathways governing the conversion process are determined through a comparison of the different production and loss rates for these value-added end products.

Keywords: atmospheric pressure; dielectric barrier discharges (DBD); gas conversion; methane; modeling

1. Introduction

Methane, the principal component of natural gas, is currently mainly used for home and industrial heating and for the generation of electrical power. On the other hand, methane is a greatly underutilized resource for the production of chemicals and liquid fuels, mainly because it is one of the most stable molecules [1]. Direct synthesis of hydrocarbons starting from methane is not yet feasible and the conventional indirect methods for partial and total oxidation of methane, which make use of a high temperature and a noble catalyst, require high amounts of energy and lack selectivity. The utilization of natural gas as a chemical resource is therefore currently limited to the production of synthesis gas by steam reforming, which is a highly energy-intensive process [2]. A sustainable process for the conversion of the abundant methane reserves into more value-added chemicals and fuels is therefore renowned as a challenge for the 21st century [1]. More in particular, the development of a process for the direct synthesis of higher hydrocarbons and oxygenates from methane in an energy-efficient way towards economy and environment would offer significant benefits [3].

Dielectric barrier discharge (DBD), can offer here a distinct advantage because they enable in a unique way gas phase reactions at ambient conditions [4]. Different plasma activation mechanisms will lead to gas heating, vibrational and electronic excitation, and ionization and dissociation of species and in this way gas conversion processes are induced.

The aim of our research is to examine the possibility of using plasma-enhanced catalysis for the conversion of CH\textsubscript{4} in the presence of oxygen, carbon dioxide or water vapor into higher oxygenates and
syngas. More specifically, our goal is to determine whether these gas conversion processes in a DBD may occur in an energy-efficient way and thus whether a process can be developed that is competitive with currently existing or emerging technologies. In order to optimize such a process to become competitive, it is essential to understand the huge underlying plasma chemistry. This is certainly the case if the purpose is to improve the selectivity of the conversion process in order to obtain a higher yield for one or more of the reaction products by using a heterogeneous catalyst acting on one or more of the underlying gas-phase reactions. Fluid modeling can provide here the necessary information to obtain insight into the gas phase chemistry that is taking place in the discharge gap.

In order to achieve our goal, we developed a 1D fluid model to describe the plasma chemistry in an atmospheric pressure DBD during the oxidation of methane. As a result, the spatially averaged densities of the various plasma species as a function of time are obtained. Furthermore, the conversion of CH$_4$ and the oxidant (O$_2$, CO$_2$), and the yields and selectivities of the reaction products are determined. Finally, this will allow us to point out the main underlying reaction pathways for the conversion of CH$_4$ into oxygenates and syngas.

2. The fluid model

The model employed in this study is a 1D fluid model called Plasimo’s MD2D [5]. The fluid model is, analogous to other fluid models used for the description of low temperature plasmas, based on a set of balance equations derived from the Boltzmann transport equation. The first equation is the species continuity equation which describes the continuity of each type of species $p$ incorporated in the model in terms of its density $n_p$, flux $\vec{\Gamma}_p$ and source $S_p$ as a function of time and space:

$$\frac{\partial n_p}{\partial t} + \nabla \cdot \vec{\Gamma}_p = S_p$$

The source term $S_p$ is obtained by considering the volume reactions in which species $p$ are produced or lost. The second equation is the drift-diffusion equation which describes the flux $\vec{\Gamma}_p$ of each type of species $p$ by means of the summation of a drift component (only for the charged species), driven by the electric field $E$, and a diffusion component, caused by the gradient of the density:

$$\vec{\Gamma}_p = \pm \mu_p E n_p - D_p \nabla n_p$$

$\mu_p$ and $D_p$ denote here the mobility and diffusion coefficient of species $p$. For the electrons also a third equation is solved. The assumption that the energy is directly related to the local electric field is not valid for electrons because they have much lower mass compared to the heavy particles. Electron parameters are therefore expressed as a function of the average energy $\overline{\epsilon}$ which results from the electron energy balance equation:

$$\frac{\partial (n \overline{\epsilon})}{\partial t} + \nabla \cdot \vec{\Gamma}_\overline{\epsilon} = S_\overline{\epsilon}$$

$S_\overline{\epsilon}$ is again a source term which depends on the heating by the electric field and on the energy gained or lost in the various reactions. $\vec{\Gamma}_\overline{\epsilon}$ denotes the electron energy flux which can be obtained from:

$$\vec{\Gamma}_\overline{\epsilon} = -\frac{5}{3} \mu_e \overline{\epsilon} E + n_e \frac{5}{3} D_e \nabla \overline{\epsilon}$$

The first term is the hydrodynamic flux of enthalpy and the second term is the heat conduction flux. This set of partial differential equations is coupled to the Poisson equation, which delivers the electric field:

$$\nabla \cdot (\varepsilon_m \nabla \varphi) = -\nabla \cdot (\varepsilon_m \vec{E}) = -\sum_p q_p n_p$$

$\varphi$ is here the electric potential as a function of time and space, $\varepsilon_m$ is the permittivity of the medium and $q_p$ is the charge of species $p$.

These equations are then solved iteratively by the so-called modified strongly implicit method in time and in space until convergence is reached. A more detailed description of the physics described in the model and of the numerical methods that are used can be found in [5-6].
In order to describe the plasma chemistry in the discharge gap in a CH\textsubscript{4}/oxidant (O\textsubscript{2}, CO\textsubscript{2}) gas mixture a consistent set of reactions involving 38 species is built up. An overview of the species taken into account in the model can be found in Table 1. All these species are provided in the model with their transport coefficients for diffusion and mobility (only for the charged species), a sticking coefficient and a secondary electron emission coefficient.

Table 1. Overview of the species taken into account in the model, besides electrons.

| Molecules | CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, H\textsubscript{2}, O\textsubscript{2}, O, CO, CO\textsubscript{2}, H\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{2}O, CH\textsubscript{3}OH, C\textsubscript{2}H\textsubscript{5}OH, CH\textsubscript{3}CHO, CH\textsubscript{3}CO, CH\textsubscript{3}OOH, CH\textsubscript{3}H\textsubscript{2}OOH |
| Ions | CH\textsuperscript{+}, CH\textsuperscript{2+}, CH\textsuperscript{3+}, CH\textsuperscript{-}, C\textsuperscript{+}, C\textsuperscript{2+}, C\textsuperscript{3+}, C\textsuperscript{-}, C\textsubscript{2}H\textsuperscript{+}, C\textsubscript{2}H\textsuperscript{2+}, C\textsubscript{2}H\textsuperscript{3+}, C\textsubscript{2}H\textsuperscript{-}, C\textsubscript{2}H\textsubscript{2-}, C\textsubscript{2}H\textsubscript{3-}, C\textsubscript{2}H\textsubscript{4+}, C\textsubscript{2}H\textsubscript{5+}, C\textsubscript{2}H\textsubscript{6+}, H\textsuperscript{+}, H\textsuperscript{-}, O\textsuperscript{+}, O\textsuperscript{-}, O\textsuperscript{2+}, O\textsuperscript{2-}, O\textsuperscript{3+}, O\textsuperscript{3-}, H\textsuperscript{2+}, H\textsuperscript{-}, H\textsuperscript{2-}, OH\textsuperscript{+}, OH\textsuperscript{-}, H\textsuperscript{+}, H\textsuperscript{-} |
| Radicals | CH\textsubscript{3}, CH\textsubscript{2}, CH, C, C\textsubscript{2}H\textsubscript{5}, C\textsubscript{3}H\textsubscript{7}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, H, O, OH, HO\textsubscript{2}, CHO, CH\textsubscript{2}OH, CH\textsubscript{3}O, CH\textsubscript{2}H\textsubscript{2}O, C\textsubscript{2}H\textsubscript{2}O, C\textsubscript{2}H\textsubscript{5}OH, C\textsubscript{3}H\textsubscript{6}OH, C\textsubscript{3}H\textsubscript{7}OH |

Figure 1. Schematic diagram of the reactor under study.

3. Reactor set-up

The numerical model is applied to an atmospheric pressure DBD (see figure 1). The reactor consists of two coaxial electrodes. The inner electrode (stainless steel) has an outer diameter of 22 mm. The outer electrode (chrome) has a diameter of 29.3 mm and at the inside it is in contact with a dielectric tube made of alumina. The alumina tube has an inner diameter of 26 mm and a wall thickness of 1.6 mm leading to a discharge gap of 2 mm wide between both cylinders. The outer electrode is powered, whereas the inner electrode is grounded. The background gas temperature is 300 K and assumed to be constant and uniform in time and space, respectively. The total length of the reactor in the experiment is 120 mm. However, in the model only a segment of 1.5 mm long is considered. Experiments are performed for this set-up to validate the calculated results.

4. Results and discussion

The calculations are carried out at a fixed applied voltage of 6 kV and a frequency of 10 kHz. Figure 2 and 3 show the spatially averaged reaction product densities as a function of the residence time in the plasma reactor for a 70/30 CH\textsubscript{4}/O\textsubscript{2} and a 70/30 CH\textsubscript{4}/CO\textsubscript{2} gas mixture, respectively. The most important end products in both cases are syngas (H\textsubscript{2} + CO), CH\textsubscript{2}O, CH\textsubscript{3}OH and H\textsubscript{2}O. Note that the formation of CH\textsubscript{3}OH is higher when O\textsubscript{2} is the co-reactant and that the formation of CH\textsubscript{2}O is higher when CO\textsubscript{2} is the co-reactant. Furthermore, it is also important to mention that in the CH\textsubscript{4}/O\textsubscript{2} gas mixture a non-negligible amount of unwanted CO\textsubscript{2} is formed.

Figure 2. Calculated densities of the reaction products, as a function of residence time in the 70/30 CH\textsubscript{4}/O\textsubscript{2} gas mixture.

Figure 3. Calculated densities of the reaction products, as a function of residence time in the 70/30 CH\textsubscript{4}/CO\textsubscript{2} gas mixture.
Figure 4 illustrates the effect of the CO\(_2\) fraction in the gas mixture on the calculated densities of the various species. It is clear that syngas is the most important end product. The H\(_2\)/CO ratio can vary from 7 (at 10 % CO\(_2\)) to 0.6 (at 90 % CO\(_2\)). Formaldehyde has a maximum formation at 30 % CO\(_2\), while CH\(_3\)OH seems to be formed most for a CO\(_2\) fraction of 50 %.

Figure 5 shows the calculated conversions of CH\(_4\) and CO\(_2\) and the yields of the various reaction products as a function of the residence time, for the 50/50 CH\(_4\)/CO\(_2\) gas mixture. After 20 s, both CO\(_2\) and CH\(_4\) appear to be converted for about 40 %. Besides C\(_2\)H\(_6\) mainly syngas is formed, in a ratio of H\(_2\)/CO equal to 1. Similar results are obtained for the other gas mixture ratios. If the CH\(_4\) content in the feed increases, mostly H\(_2\) and C\(_2\)H\(_6\) are formed. On the other hand, if the CO\(_2\) content in the feed increases, mostly syngas is formed.

The most important pathways for the production and consumption of formaldehyde (CH\(_2\)O) for the 70/30 CH\(_4\)/CO\(_2\) gas mixture are illustrated in figure 6. CH\(_2\)O is mainly formed by:

\[
\text{CH}_2 + \text{CO} \rightarrow \text{CH}_2\text{O} + \text{CO} \quad (R1)
\]

The loss of CH\(_2\)O is mainly attributed to the following reactions:

\[
\begin{align*}
\text{O} + \text{CH}_2\text{O} & \rightarrow \text{OH} + \text{CHO} \quad (R2) \\
\text{OH} + \text{CH}_2\text{O} & \rightarrow \text{H}_2\text{O} + \text{CHO} \quad (R3) \\
\text{H} + \text{CH}_2\text{O} & \rightarrow \text{H}_2 + \text{CHO} \quad (R4)
\end{align*}
\]

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