Dielectric barrier discharges used for the conversion of greenhouse gases: modeling the plasma chemistry by fluid simulations
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Dielectric barrier discharges (DBDs) are gaining increasing interest for environmental applications. The topic we have investigated is the conversion of greenhouse gases (CH₄, CO₂) into value-added chemicals, such as syngas (H₂+CO), methanol (CH₃OH) or formaldehyde (CH₂O). These greenhouse gases are inert, hence conversion into other chemicals requires high temperature and pressure by classical methods, such as dry reforming and steam reforming. The latter processes are therefore very energy-intensive. Non-LTE plasmas, such as DBDs, can provide a solution for this, as they are characterized by highly energetic electrons, whereas the gas itself is near room temperature. The electrons collide with the gas molecules, thereby creating ions, radicals and excited species, which can react to form new molecules. This enables reactions that would thermodynamically not occur at room temperature. Therefore, DBDs could provide an interesting alternative for the conversion of greenhouse gases, at least if the electric energy needed to sustain the plasma is reasonable; the latter still needs to be investigated in more detail.

To optimize the conversion of CH₄ and CO₂ into syngas and oxygenates like methanol and formaldehyde, computer modeling of the plasma chemistry is very useful. In this presentation, we will show calculation results of fluid modeling, carried out for a DBD operating in a mixture of CH₄ with O₂ and with CO₂.

The fluid model used for this purpose is the so-called MD2D model, which forms part of the PLASIMO code, developed at Eindhoven University of Technology [1]. For every plasma species included in the model (see Table 1), a continuity equation and a transport equation are constructed. The continuity equation is a balance equation with different production and loss terms, as defined by the chemical reactions. The transport equation is based on diffusion due to concentration gradients and drift in the electric field (for the charged species). Furthermore, an energy balance equation is solved for the electrons, to account for the energy gain from the electric field and the energy losses due to collisions. For the other plasma species, the so-called heavy particles, no energy balance equation needs to be solved, as they can be considered in thermal equilibrium with the gas. Finally, these equations are coupled to Poisson’s equation, in order to obtain a self-consistent electric field distribution.
The different plasma species listed in Table 1 can react with each other, making the plasma a complex chemical reactor. In total, 138 electron-impact reactions (i.e., ionization, electronic and vibrational excitation, dissociation, attachment, …), 41 electron-ion recombination reactions, and 540 heavy particle reactions (i.e., ion-ion, ion-neutral and neutral-neutral reactions) are included in the model. The same plasma species and chemical reactions are considered in both gas mixtures, as CO$_2$ is also formed as a plasma species in the CH$_4$/O$_2$ gas mixture, and vice versa, O$_2$ is formed in the CH$_4$/CO$_2$ gas mixture.

The calculations are performed for a cylindrical DBD reactor, as illustrated schematically in figure 1. It consists of two concentric electrodes, made of stainless steel. Both electrodes are The outer electrode is covered with a 1.6 mm thick dielectric layer (alumina). It is powered, whereas the inner electrode is grounded. The gap between both cylinders, i.e., the region where the gas flows through the reactor, is 2 mm.
Typical calculation results include the densities of the various plasma species formed, information about their important production and loss mechanisms, as well as the conversion of the reactant gases, and the yields and selectivities of the reaction products. Calculations are performed for a wide range of operating parameters, such as gas ratio, electric power, applied frequency, gap width and dielectric material, to investigate the best operating conditions for maximum conversion and yields. Also the optimum residence time for maximum yields of the desired products is predicted.

Figure 2 illustrates the calculated conversion of CH₄ and CO₂, and the yields of the various reaction products, for a CH₄/CO₂ gas mixture of 90/10, at an applied voltage of 6 kV and frequency of 10 kHz. A similar result is presented in figure 3 for a CH₄/CO₂ gas mixture of 70/30, at the same applied voltage and frequency. At 90/10, CO₂ is converted after about 10 s, whereas it takes roughly 20 s before CH₄ is converted. The reaction products are the higher hydrocarbons (C₂H₂, C₂H₄, C₂H₆) as well as H₂ and CO, i.e. syngas, in a ratio of about 4/1. At 70/30, both CH₄ and CO₂ are not yet fully converted after 20 s. The major reaction products are now CO and H₂ in a ratio of about 50/50. Besides the higher hydrocarbons, also CH₂O and H₂O are formed, although their yield is only a few % after 20 s (see right part of figure 3).

Fig 2: Calculated conversion of CH₄ and CO₂, and yields of the most important reaction products, in a gas ratio of 90/10, at an applied voltage of 6 kV and frequency of 10 kHz.

Fig. 3: Calculated conversion of CH₄ and CO₂, and yields of the most important reaction products, in a gas ratio of 70/30, at an applied voltage of 6 kV and frequency of 10 kHz.
Figure 4 and 5 present the calculated conversions of CH₄ and O₂, and the yields of their major reaction products, for a CH₄/O₂ mixture of 90/10 and 70/30, respectively, at the same applied voltage and frequency of 6 kV and 10 kHz. It is clear from figure 4 that O₂ is very quickly converted, i.e. after only a few seconds, in the 90/10 reaction mixture. This behaviour is reflected in the yields of the reaction products, i.e., after a few seconds the yields of the oxygen-containing reaction products already reach their maximum, as the O₂ is all consumed. Besides the reaction products found in the CH₄/CO₂ mixture, also methanol (CH₃OH) is formed, although its yield reaches only a few %, and drops again after a few seconds, when all O₂ is consumed. In the 70/30 mixture, O₂ is also much faster converted than CH₄, but at least it takes more than 10 s, so that the oxygen-containing reaction products can reach somewhat higher yields, as appears from figure 5.

Fig. 4: Calculated conversion of CH₄ and O₂, and yields of the most important reaction products, in a gas ratio of 90/10, at an applied voltage of 6 kV and frequency of 10 kHz.

Fig. 5: Calculated conversion of CH₄ and O₂, and yields of the most important reaction products, in a gas ratio of 70/30, at an applied voltage of 6 kV and frequency of 10 kHz

Reference