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FLUID MODELING OF THE CONVERSION OF CH_4 IN THE PRESENCE OF O_2 OR CO_2 INTO METHANOL AND SYNGAS IN AN ATMOSPHERIC PRESSURE DIELECTRIC BARRIER DISCHARGE

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The world primary energy demand will increase by 1.6% per year on average from 2006 to 2030. The worldwide non-renewable energy resources are however finite and it becomes more difficult to recover them [1]. Therefore a growing need is being imposed for a global sustainable energy strategy based on an improvement of the energy efficiency of the current technologies and a more intensifying diversification of the energy resources with a huge preference for lower carbon resources.

Methane, the principal component of natural gas, has still a significant growth potential and it becomes more and more an interesting alternative for crude oil as feedstock for the chemical industry. It is currently mainly being used for home and industrial heating and for the generation of electrical power. On the other hand methane is greatly underutilized for the production of chemicals and liquid fuels, mainly because it is one of the most stable molecules [2]. Direct synthesis of hydrocarbons starting from CH_4 is not yet feasible and the conventional indirect oxidation methods have poor yields and require high amounts of energy [3].

A sustainable process for conversion of the abundant methane reserves into more value-added chemicals and fuels is therefore renowned as a challenge for the 21st century [2]. More in particular, the development of a process for the direct synthesis of higher hydrocarbons and oxygenates from methane in an energy-efficient way would offer significant benefits.

Atmospheric pressure non-thermal plasmas, such as dielectric barrier discharges (DBDs), 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 act causing vibrational and electronic excitation, and ionization and dissociation of species and in this way gas conversion processes are induced. These processes always involve a huge underlying plasma chemistry and in order to improve such a process, it is indispensable to get notion of the play of the different species in the immensity of chemical reactions. Fluid modeling can provide here the necessary information to obtain insight in the gas phase chemistry that is going on in the discharge gap.

In particular, the conversion of CH_4 in the presence of O_2 and CO_2 into methanol and syngas has been investigated. Therefore a two-dimensional time-dependent fluid model for an atmospheric pressure cylindrical DBD, called Plasimo's MD2D [5], has been applied. The fluid model is, analogous to other fluid models used for the description of low temperature plasmas, based on the continuity and flux equations for each type of species treated, the electron energy equation and the Poisson equation. This set of coupled partial differential equations is solved by the so-called modified strongly implicit method. Details of the model can be found in [6].

The reactor consists of two coaxial stainless steel electrodes. The outer one, which is covered with a dielectric, is powered and the inner one is grounded. The amplitude and frequency of the applied voltage and the inlet gas ratios have been varied. In order to describe the complete chemistry in a CH_4/O_2 or in a CH_4/CO_2 plasma 67 species are taken into account in the model (Table 1). A consistent set of 692 gas phase reactions is built up to describe the plasma chemistry in the discharge gap. These reactions can be divided into four groups: 126 electron-neutral, 39 electron-ion, 347 neutral-neutral and 180 ion-ion/neutral reactions. The rates of the different reactions are calculated in the model from the densities of the colliding species and the related reaction rate coefficients. For the electron-induced reactions, cross sections as a function of the electron energy were defined as input for the Boltzmann solver BOLSIG+ [6], which provides for the energy dependent transport and rate coefficients, whereas the neutral-neutral and the ion-ion/neutral reactions were characterized by a constant reaction rate coefficient for the working pressure and temperature of 1 atm and 300 K, respectively.

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

Molecules	Ions	Radicals
CH_4	CH_5^+, CH_4^+, CH_3^+, CH_2^+, CH^+, C^+	CH_3, CH_2, CH, C
C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6	$C_2H_6^+$, $C_2H_5^+$, $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, C_2H^+, C_2^+	C_2H_5, C_2H_3, C_2H, C_2, C_3H_7, C_3H_5
H_2	H_3^+, H_2^+, H^+	H
O_3, O_2	O_4^+, O_2^+, O^+, O_4^-, O_3^-, O_2^-, O^-	O
CO_2, CO		
H_2O, H_2O_2		OH, HO_2
CH_2O, CH_3OH, C_2H_5OH, CH_3CHO, CH_2CO, CH_3OOH, C_2H_5OOH		CHO, CH_2OH, CH_3O, C_2H_5O, C_2HO, CH_3CO, CH_2CHO, CH_3O_2, $C_2H_5O_2$

In this way amongst others density profiles and fluxes of all the different plasma species, as well as the relative importance of their various production and loss processes, have been obtained for the two different gas mixtures. Moreover, the conversion of CH_4 and the yields and selectivities of the various reaction products for the different operating conditions have been calculated. The optimal plasma parameters (gas ratio, applied frequency and amplitude, residence time, …) will be pointed out for the two gas mixtures in order to reach an optimum yield and selectivity, and the gas mixtures will be compared mutually.

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