Conversion of Methane to C_2 Hydrocarbons and Hydrogen Using Microwave ´tornado´-type Plasma

D. Tsyganov, N. Bundaleska, E. Tatarova

Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico,

Universidade de Lisboa, Lisboa, Portugal

A microwave (2.45 GHz) "tornado" - type plasma with a high-speed tangential gas injection (swirl) working at atmospheric pressure conditions has been applied for reforming of methane. Theoretical model based on a set of nonlinearly coupled, spatially dependent differential equations describing plasma thermodynamics, gas heating and flow has been developed.

Keywords: microwave plasma, methane, hydrogen.

Introduction.

The interest in reforming technologies for hydrogen production is motivated by the ongoing need for energy and environmental pollution. As well hydrogen has the potential to effectively reduce our dependence on fossil fuels, since it is present in compounds such as water, hydrocarbons, biomass, etc. Among different conversion technologies - steam reforming, partial oxidation and autothermal reforming - steam methane reforming is the most common commercially used method for hydrogen production [1, 2]. Plasma systems offer an adequate solution to this problem since plasma comprises thermal and chemical reactor functions, as well as, catalytic properties.

Microwave plasma operating at atmospheric pressure demonstrates important advantages compared to other plasma sources as a conversion tool, since it can achieve extremely high densities of active species of interest at relatively low gas temperatures [3].

In this study, a surface wave driven microwave plasma operating at atmospheric pressure conditions has been applied for reforming of methane. The optical emission spectrum in the range 250-700 nm has been investigated to detect the presence of the species of interest in the plasma. Kinetic model describing the methane decomposition in the argon plasma environment have been proposed.

Experimental setup.

Surface-wave driven plasma is a special type of microwave plasma where the microwave power is transferred to the plasma by the electric field of a guided wave [3]. The scheme of the experimental setup is shown in Fig. 1 along with the swirl injector and a photo of the plasma torch. Microwaves at 2.45 GHz are provided by a generator with maximum power of 2 kW. The microwaves travel through a waveguide system, which includes a water-cooled

circulator, directional couplers, a 3-stub tuner, a moveable short-circuit and a waveguide surfatron as a field applicator.

The discharge ignites in a quartz tube, placed vertically and perpendicularly to the waveguide wider wall. The injected into the discharge gas mixture consists of premixed argon and methane. The total gas flow introduced into the discharge was $Q^{tot} = Q_{Ar} + Q_{CH4}$. The microwave power was kept P = 500 W, argon flow Q_{Ar} = 250 sccm and methane flow Q_{CH4} = 0.6 sccm. The discharge is sustained under vortex-type flow conditions, which are provided by a swirl system (Fig. 1b). Relative concentration of C_2, H_2 and H were monitored using OES.

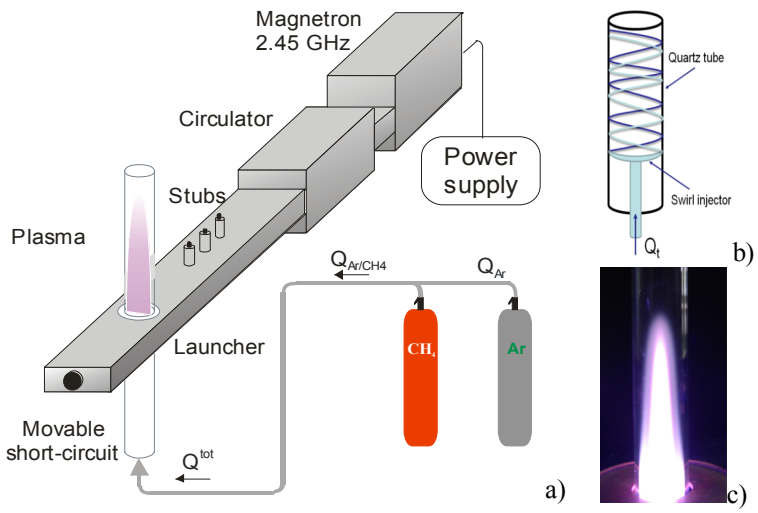

Fig 1. Scheme of the experimental setup (a), sketch of the swirl system (b) and a photo of the plasma torch (c)

Theoretical model.

The "active" microwave plasma region of the reactor considered is composed of two zones. The first one is the surface wave sustained discharge zone, including the zone inside the launcher and the extended "hot" plasma zone outside the launcher. Here, the surface wave power is absorbed by plasma electrons, which transfer the power to heavy particles via elastic and inelastic collisions, resulting in high gas temperatures. The gas temperature maintains nearly constant in the discharge zone when moving away from the launcher (up to about 10 cm) and then drops sharply in the "near" (10 - 13 cm) afterglow plasma zone. The second zone in axial direction is plasma afterglow (~20 cm) zone. The model input parameters are externally controlled, i.e. gas flows, total power delivered to the launcher, pressure and background gas mixture composition, i.e. Ar/CH_4 injected into the discharge.

A kinetic scheme similar to that presented in [4] is used. The scheme includes 57 components and about 390 chemical reactions. The model was applied for the heterogeneous case, i.e. considering that both gas and solid phase carbon nuclei are formed in the plasma. The gas thermal balance equation can be written as: $\frac{p_0}{k_{Bol}} V_0 \frac{1}{T_0} C_p \frac{dT_a}{dz} = -\frac{4\chi(T)}{R^2}(T_a - T_w) + \frac{\delta}{S}\frac{dP}{dz}$ here V_0 - initial gas velocity [m/s], T_0 - initial

gas temperature, p_0 - gas pressure, k_{Bol} - Boltzmann's constant, $C_p = 5/2k_{Bol}$, S - plasma cross-section and P - absorbed microwave power, δ - coefficient expressing the fraction of absorbed power. (LLA: Some quantities are not defined)

Results and discussion.

The equilibrium values of the stable substances and intermediate complexes along the "hot" plasma zone are useful to understand the general workings of methane decomposition and formation of carbon precursors. The calculated equilibrium values, i.e., the calculated concentrations of the main substances are shown in Fig. 2a and 2b as a function of the gas temperature. The equilibrium dissociation of methane begins at around 500 K and is complete at 1000 K. If the equilibrium heterogeneous process is considered, solid carbon and molecular hydrogen are the products formed in the range 1000 – 2500 K. Further, hydrogen dissociates and acetylene formation begins, reaching maximum concentration at ~3000 K.

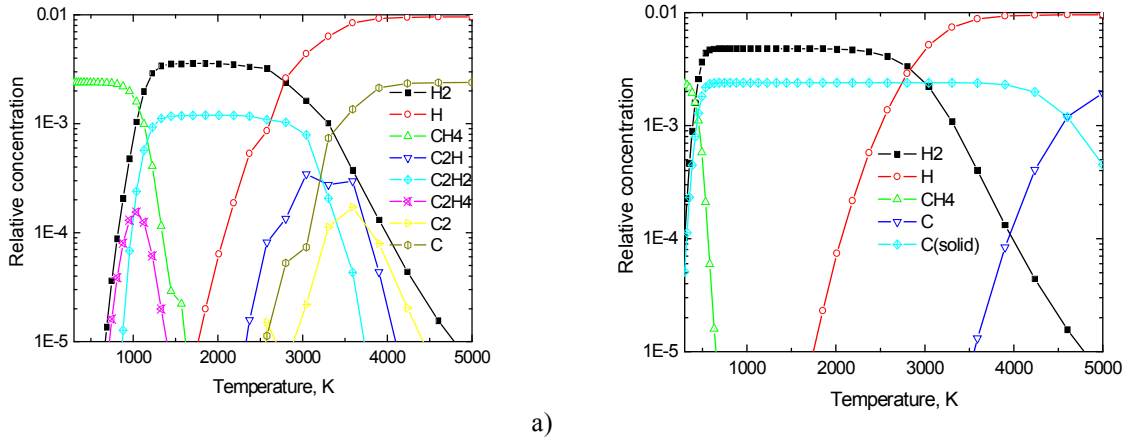

Fig 2. Simplified equilibrium homogenous (a) and equilibrium heterogeneous (b) diagrams for the main methane decomposition products

The non-equilibrium results presenting the axial distribution of the decomposition products for heterogeneous case are shown in Fig. 3. Methane dissociation begins in "hot" plasma zone (~ 0.5 cm). The major initial reaction is C-H bond breaking with simultaneous formation of CH_3, CH_2, CH, H, C_2 and C at "hot" plasma zone. These radicals are involved in the formation of ethane and ethylene. The recombination of radicals can lead to the formation of acetylene through the following reactions:

$$CH_3 + CH_3 \rightarrow C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + 2H_2, \quad CH_2 + CH_2 \rightarrow C_2H_4 \rightarrow C_2H_2 + H_2,$$

$$CH + CH \rightarrow C_2H_2, \; CH_3 + CH \rightarrow C_2H_2 + H_2, \; CH_2 + CH \rightarrow C_2H_2 + H.$$

The acetylene is a stable molecule and can be broken down to the simplest C and H atoms at sufficiently high temperatures (above 4000 K). Diffusion of gas-phase carbon takes place

from the "hot" plasma zone towards the tube wall, where the temperature is lower and nucleation of carbon species takes place. The main zone where nucleation occurs is located near the tube walls. (LLA: repetition) Part of the solid carbon nuclei is deposited on the wall; however the major part is gradually removed with the outlet gas stream.

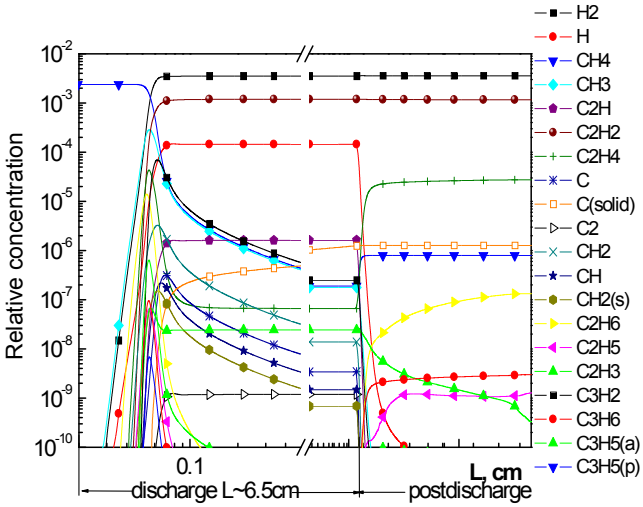

Fig 3. Simplified nonequilibrium heterogeneous diagram for the main methane decomposition products.

Conclusion.

A microwave, "tornado"-type plasma, with swirl injection of the background gas, operating at 2.45 GHz and atmospheric pressure has been used to decompose methane in argon and argon-water vapor plasma environments. The theoretical model based on a set of non-linear rate balance equations describing the chemical kinetics and the gas thermal balance has been developed. Hydrogen, solid carbon and acetylene are the main outlet products. Production of acetylene can be promoted by preventing the formation of carbon. The results of the present investigation clearly show that surface wave sustained microwave plasma is a promising tool for methane reforming. Further investigation is in progress to analyze in detail the carbon balance, including measurements of the carbon deposited on the walls as well as the solid carbon carried away by the outlet gas flow.

Acknowledgments.

This work was supported by the Fundação para a Ciência e Tecnologia (FCT) under projects PTDC/FIS/108411/2008 and Pest-OE/SADG/LA/0010/2011.

References.

1. *Lange J.P., Jong K.P., Ansorge J., Tijm P.J.A.* Studies in Surface Science and Catalysis 1997. V.107 doi:10.1016/S0167-2991(97)80320-5
2. *Dias F.M., Bundaleska N., Henriques J., Tatarova E., Ferreira C.M.* Journal of Physics Conference Series Issue 06. 2014. doi:10.1088/1742-6596/516/1/012002
3. *Tatarova E., Bundaleska N., Dias F. M., Tsyganov D., Saavedra R. and Ferreira C. M.* Plasma Source Sciences and Technology V22. 2013. doi:10.1088/0963-0252/22/6/065001
4. *Bundaleska N., Tsyganov D., Tatarova E., Dias F.M., Ferreira C.M.* International Journal of Hydrogen Energy Vol.11 2014. Issue 39. doi:10.1016/j.ijhydene.2014.01.194