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ORIGINAL PAPER

# Methane cracking and secondary hydrocarbon generation in inductively coupled RF plasmas

**Francisco L. Tabarés,**
**Daniel Alegre,**
**Miran Mozetič,**
**Alenka Vesel**

**Abstract.** Pure methane plasmas have been produced in an inductively coupled radio frequency (ICRF) reactor with quartz walls in the absence of carbon film deposition. A differentially pumped mass spectrometer was used for the recording of the secondary hydrocarbon species produced in the reactor. The functional dependences of these species with plasma parameters has been analyzed and tentative mechanisms for their formation have been formulated. High power per molecule ratio promotes methane decomposition and acetylene formation.

**Key words:** plasma • RF discharges • hydrocarbon cracking • methane reforming • plasma-assisted chemical vapour deposition (PACVD) • carbon films

F. L. Tabarés✉, D. Alegre
Laboratorio Nacional de Fusion,
Centro de Investigaciones Energéticas,
Medioambientales y Tecnológicas (CIEMAT),
22 Avda Complutense, E-28404 Madrid, Spain,
Tel.: +91 346 6458, Fax: +91 346 6124,
E-mail: tabares@ciemat.es

M. Mozetič, A. Vesel
Department of Surface Engineering,
Jožef Stefan Institute,
39 Jamova Str., SI-1000 Ljubljana, Slovenia

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## Introduction

Hydrocarbon decomposition in technical plasmas is an interesting issue with applications in diamond like film deposition, hydrogen synthesis by methane reforming and nanocarbon technology, to mention a few [2]. Very different results may be obtained depending on the plasma characteristics, type of hydrocarbon, substrate characteristics, etc. Moreover, the continuous evolution of the wall status as the film is being deposited and the associated heterogeneous elemental reactions mediated by the surface add extra complexity to the system and makes steady state conditions hard to reach [5]. In this work, the destruction of methane in a low pressure, electrodeless radio frequency (RF) discharge was studied by mass spectroscopy. Plasmas were created in a quartz tube, of well-known low radical sticking characteristics. The discharge parameters were chosen in such a way that plasma appeared in either E or H mode [6]. The transition between the modes is abrupt and is easily observed with a naked eye since the luminosity of plasma is several orders of magnitude larger in the H than in the E mode. The evolution of different hydrocarbon species vs. discharge power was measured systematically by a differentially pumped mass spectrometer. No carbon deposit on the quartz walls was seen during the scans. The results showed that the destruction of methane depends on the flow rate as well as the discharge power and was accomplished already in the E mode. Well-pronounced maxima in the formation of both ethane and acetylene were observed at low gas flow rates. The observed products from radical recombination evolved

with plasma conditions, and their contribution to the global carbon balance strongly decreased at high power per particle molecule. The functionality of secondary hydrocarbon formation with respect to the experimental parameters has been analyzed and a simple kinetic model has been developed, but not shown in this work due to space constrains.

## Experimental results

Experiments were performed in the RF reactor schematically presented in Fig. 1 and is shown in more detail elsewhere [3]. The system is pumped with a two stage rotary pump with the pumping speed of 80 $m^3$/h. Methane of commercially available purity is introduced into the discharge chamber made from quartz. The outer diameter of the discharge chamber is 40 mm, while the inner diameter is 36 mm. The length of the chamber is 40 cm. The discharge chamber narrows to a quartz tube with the inner diameter of 3 mm and length of 40 mm to prevent propagation of charged particles and radicals into the afterglow chamber and to allow for a rapid drop of pressure. Namely, the plasma is created at the pressure of a few mbar (depending on the gas flow), while the pressure in the afterglow chamber is more than an order of magnitude lower. The afterglow chamber terminates with a collimator that is mounted in order to allow for appropriate pressure in the mass spectrometer (MS) and its main function is to keep the mass spectrometer free from disturbance by the RF source. The mass spectrometer was a well-calibrated residual gas analyzer (SRS-RGA200) that was pumped with a 250 l/s turbomolecular pump backed by an 8 $m^3$/h two stage rotary pump to a base pressure of $< 2 \times 10^{-7}$ mbar. The system is high vacuum compatible (copper gaskets are used) and almost leak-free, but it has never been baked. The mass spectra were taken in the mass range from 0 to 40. The total pressure at the RGA during experiments was kept below $5 \times 10^{-5}$ mbar.

Methane was continuously leaked into the discharge chamber and pumped away during the experiments. There is a coil of 6 turns mounted onto the discharge chamber as shown in Fig. 1. The coil is connected to the matching network and the network is connected to a radio frequency generator. The RF generator operates at the standard frequency of 13.56 MHz and the nominal power (i.e. the power read on the generator screen) up to 1200 W. The standard matching network consisting of 2 capacitors was manually adjusted to match the H mode of the discharge. Therefore, the discharge is mismatched in the E mode. The power is then always referred to the nominal power of the generator and not to the forwarded power. In the E mode, the forwarded power is much smaller than the nominal value, while in the H mode the forwarded power is more than 90% of the nominal one. The forward power was determined by measuring the coil voltage and current with an oscilloscope as described in [6]. The reactor chamber was actively cooled by forced air and cooling water was forced through the coil. Wall temperature was recorded during the experiments, and a maximum increment of 100°C for the highest injected RF powers was measured. Methane flows between 1.16 and 3.30 mbar·l/s and various RF powers up to 1200 W were used. Depending on the gas flow and RF power, the discharge was either in E or H mode.

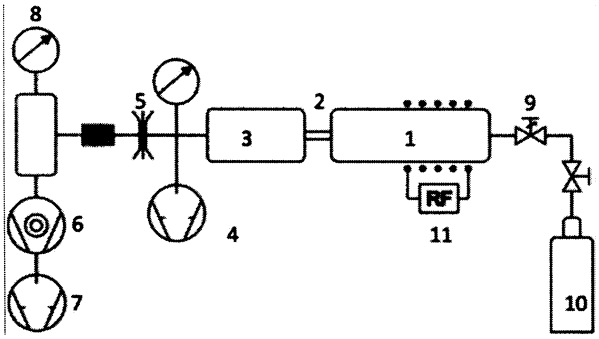


**Fig. 1.** Scheme of the experimental set-up. 1 – discharge chamber; 2 – narrow glass tube; 3 – afterglow chamber; 4 – rotary pump 80 $m^3$/h; 5 – orifice; 6 – turbomolecular pump; 7 – rotary pump 8 $m^3$/h; 8 – mass spectrometer; 9 – inlet valve; 10 – methane flask; 11 – RF generator with matching unit.

Different flow rates and nominal powers were used for the experiments, corresponding to power density values from 5 to 150 eV/molecule. As an example of direct measurements, Figure 2 displays the evolution of the most significant mass spectrometric peaks vs. the nominal power of the RF generator at the flow rate corresponding to a flow setting of 15 Pa (3.30 mbar·l·$s^{-1}$). While peaks at amu 15 and 16 decrease in parallel as the power is increased, the formation of $C_2$ hydrocarbons and molecular hydrogen can be identified through the corresponding mass spectrometric peaks. The power scan was repeated at several settings of the mass flow regulator. Only the pressure at the entrance of the pump was directly recorded. The resulting pressures inside of the reactor, $P_1$, were evaluated from the injected flows and the conductance, $C$, of the narrow tube connecting the discharge and afterglow chambers shown in Fig. 1. Under the viscous flow approximation and for nitrogen it reads [$C$ (l/s) = $180 \cdot (d^4/l) \cdot (P_1/2)$] and $Q$ (torr·l/s) = $P_1 \cdot C$ (l/s), where $l$ is the length of the reactor chamber (20 cm) and $d$ its diameter (1.8 cm) and $P_1 >> P_3$ is assumed. Also, from the known volume of the plasma region ($V_1$ = 200 cc), the corresponding residence times ($\tau_r$(s) = $V/C$) were deduced. Table 1 summarizes

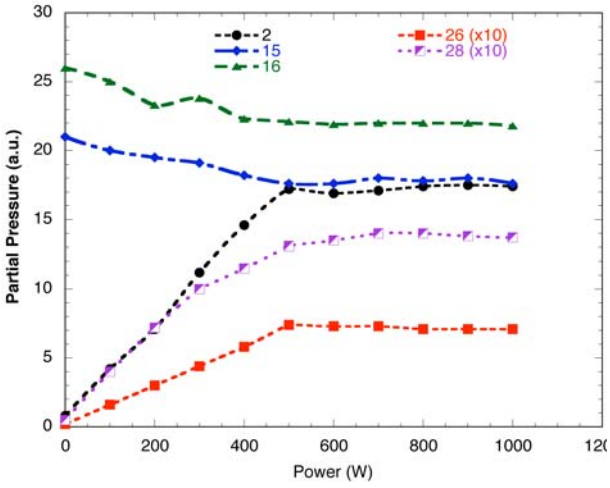


**Fig. 2.** An example of the dependence of some mass spectrometric peaks vs. the nominal power of RF generator at the methane flow setting of 15 Pa.

**Table 1.** Vacuum parameters of the experiments here reported

| Flow setting (Pa) | $Q$ (mbar·l/s) | Seff (l/s) | $P$ reactor (mbar) | Residence time (s) |
|---|---|---|---|---|
| 6 | 1.16 | 0.40 | 2.90 | 0.50 |
| 7 | 1.52 | 0.45 | 3.30 | 0.44 |
| 8 | 1.73 | 0.50 | 3.65 | 0.40 |
| 10 | 2.20 | 0.54 | 3.95 | 0.37 |
| 15 | 3.30 | 0.67 | 4.90 | 0.30 |

the vacuum parameters corresponding to the different settings used in this work.

The recombination, either homogeneous or on the walls, of the free radicals produced by the decomposition of methane leads to the formation of high order hydrocarbons. Mass spectra in the range of amu < 40 were systematically recorded, so that only $C_2H_x$ species were detected within the limited range of the mass spectrometric scans. Due to the complex chemistry of the system, a deep insight into the underlying mechanism of hydrocarbon cracking and plasma film deposition can only be achieved through the deconvolution of the mass spectra to yield the individual contribution of the different product species. For this purpose, the known contribution of each $C_2$ species to the MS peaks in the range from amu 25 to amu 30 was introduced into a simple reconstruction algorithm [1]. An excellent agreement between the calculated and recorded signal intensities was obtained, thus precluding any significant contribution from $C_3$ hydrocarbons and from non-hydrocarbon species ($N_2$ and CO) to the recorded spectra. In Fig. 3, the dependence of the resulting $C_2$ hydrocarbon composition on the injected power is displayed for two flow settings. Basically, at low cracking fractions of methane, ethane is the dominant species, while relatively high fractions of acetylene are produced under high cracking plasma conditions. Interestingly, ethylene is always rather marginal in the products composition. It must be pointed out here that a more direct discrimination among the products was possible in a previous work by using the cryotrap-assisted mass spectrometry (CTAMS) technique [4], in direct current (DC) glow discharge methane plasma under carbonized walls, i.e., after coating the reactor walls with a plasma-generated a-C:H film. In that case, under the presence of a permanent carbon film and ion bombardment, acetylene strongly dominated the $C_2$ product composition with a non-negligible contribution from ethylene. In order to check for the correlation existing between a carbonated wall and the strong production of acetylene, some experiments were intentionally performed at longer times and high power/molecule values (H mode). A carbon film was then produced, as visually verified. Figure 4 shows the time evolution of the mass spectra signals during the film deposition. Note the continuous rise of acetylene production at constant cracking fraction of methane, indicating the contribution of the film itself to the formation of this unsaturated hydrocarbon. Contrary to the case shown in Fig. 3a, the ratio of acetylene to ethane concentration reaches values well over 1.

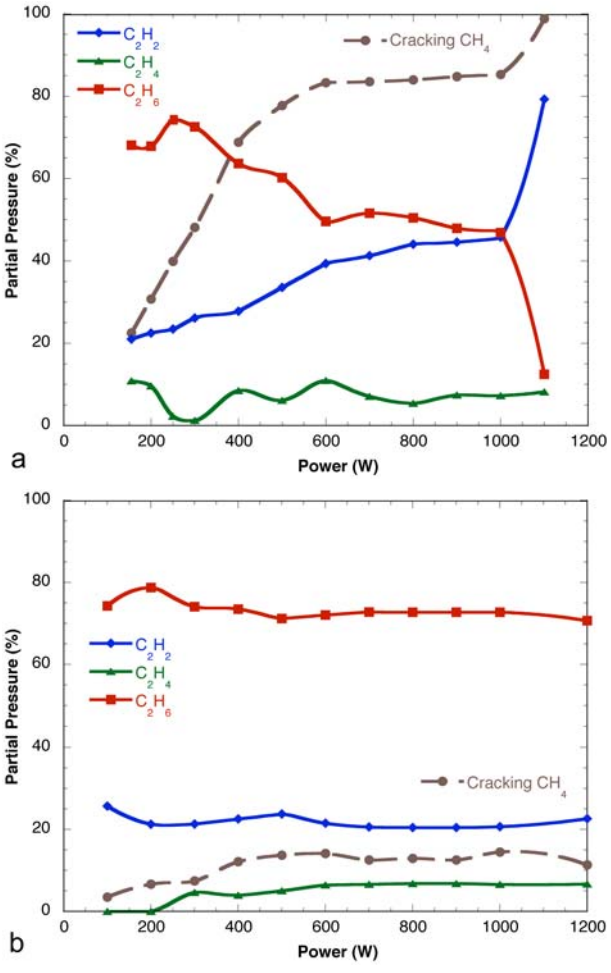


**Fig. 3.** Fractional contribution of $C_2H_x$ ($x$ = 2, 4, 6) hydrocarbons to the total reaction products at two methane flow settings: (a) 8 Pa; (b) 15 Pa. Also shown is the fraction of injected methane cracked by the discharge (referred below to as $\Delta CH_4$).

As seen in Fig. 3, strong differences appear in the composition of products as the power per molecules is decreased from the 8 to the 15 Pa case. Thus, for example, if methane reforming by ICRF plasma in the absence of carbon deposits were to be pursued, low

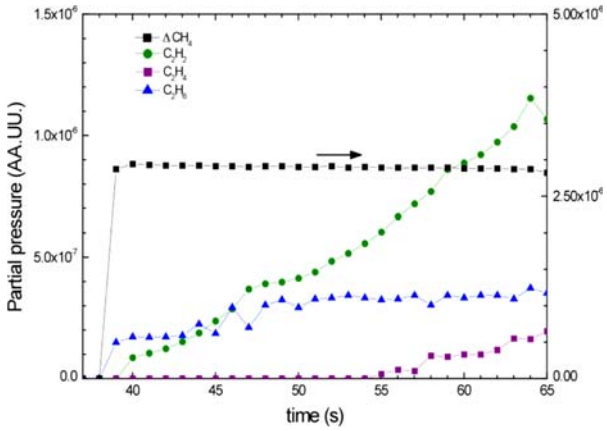


**Fig. 4.** Evolution of $C_2H_x$ hydrocarbons as a carbon film is deposited on the reactor walls.

flows and high powers will favour the degree of cracking and formation of hydrocarbons with low H content, i.e., optimal $H_2$ formation yield. Finally, a simple kinetic model based on radical recombination and gas phase reactions has been developed to account for the results obtained in the present work and be published elsewhere.

## Summary and conclusions

The decomposition of methane and the concomitant formation of $C_2$ hydrocarbons have been investigated in an ICRF in the absence of film deposition. Ample variation of the main external parameters (gas flow and injected power) was achieved. Strong changes on the cracking efficiency and on the chemical composition of the products were observed. H mode discharges, corresponding to high energy/molecule values, promote the formation of acetylene by-products respect to other $C_2$ hydrocarbons.

## References

1. Davis JW, Haasz AA, Stangeb JP (1988) Hydrocarbon formation due to combined $H^+$ ion and $H^0$ atom impact on pyrolytic graphite. J Nucl Mater 155/157:234–240
2. Silva SRP (ed) (2003) Properties of amorphous carbon. INSPEC, London
3. Tabarés FL, Ferreira JA, Ramos A *et al*. (2010) Suppression of tritium retention in remote areas of ITER by nonperturbative reactive gas injection. Phys Rev Lett 105:175006
4. Tabarés FL, Ferreira JA, Tafalla D (2007) On the mechanism of nitrogenated carbon film deposition by PACCVD in the presence of nitrogen. A cryo-trapping assisted mass spectrometric study. Chem Vapor Depos 13:335–344
5. Yamada R (1990) Enhancement of $C_2H_2$ formation due to interaction of graphite with energetic protons. J Nucl Mater 174:118–120
6. Zaplotnik R, Vesel A, Mozetic M (2011) Transition from E to H mode in inductively coupled oxygen plasma: hysteresis and the behaviour of oxygen atom density. Europhys Lett 95:55001-5