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 m³/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 m³/h two stage rotary pump to a base pressure of \(< 2 \times 10^{-7} \text{ mbar}\). The system is high vacuum compatible elsewhere [3]. The system is pumped with a two stage rotary pump 80 m³/h; 5 – orifice; 6 – turbomolecular pump; 7 – rotary pump 8 m³/h; 8 – mass spectrometer; 9 – inlet valve; 10 – methane flask; 11 – RF generator with matching unit.

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 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 m³/h two stage rotary pump to a base pressure of \(< 2 \times 10^{-7} \text{ mbar}\). The system is high vacuum compatible elsewhere [3]. The system is pumped with a two stage rotary pump 80 m³/h; 5 – orifice; 6 – turbomolecular pump; 7 – rotary pump 8 m³/h; 8 – mass spectrometer; 9 – inlet valve; 10 – methane flask; 11 – RF generator with matching unit.

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

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 C₂Hₓ 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 C₂ 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 C₃ hydrocarbons and from non-hydrocarbon species (N₂ and CO) to the recorded spectra. In Fig. 3, the dependence of the resulting C₂ 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 cryotraps-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 C₂ 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.

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

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Table 1. Vacuum parameters of the experiments here reported

<table>
<thead>
<tr>
<th>Flow setting (Pa)</th>
<th>Q (mbar·l/s)</th>
<th>Seff (l/s)</th>
<th>P reactor (mbar)</th>
<th>Residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.16</td>
<td>0.40</td>
<td>2.90</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>1.52</td>
<td>0.45</td>
<td>3.30</td>
<td>0.44</td>
</tr>
<tr>
<td>8</td>
<td>1.73</td>
<td>0.50</td>
<td>3.65</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>2.20</td>
<td>0.54</td>
<td>3.95</td>
<td>0.37</td>
</tr>
<tr>
<td>15</td>
<td>3.30</td>
<td>0.67</td>
<td>4.90</td>
<td>0.30</td>
</tr>
</tbody>
</table>

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Fig. 3. Fractional contribution of C₂Hₓ (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 ΔCH₄).

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Fig. 4. Evolution of C₂Hₓ 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\textsubscript{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\textsubscript{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\textsubscript{2} hydrocarbons.

### References