

Coupling and reforming of methane by means of low pressure radio-frequency plasmas

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Abstract

Non-oxidative coupling of CH₄/H₂ mixtures was carried out by means of radio frequency (rf) glow discharges for the first time. A central composite design was employed to determine the best experimental conditions for methane transformation into higher hydrocarbons and to fit the experimental data. rf power was the factor showing the highest effect on the results while CH₄/H₂ mole ratio showed the lowest. Conversion was 46.4% at 100 W, 0.07 mbar and CH₄/H₂ mole ratio of 1/2. Selectivity was 56.9% for C₂, 6.9% for C₃, and 36.2% for C₄ hydrocarbons. Least squares fits of quadratic equations yielded approximating functions permitting to predict results of random experiments with errors of about 5%. The same rf system was used for the reforming of methane with CO₂, O₂, and steam plasmas, respectively. The highest oxidation was observed with oxygen whilst steam plasma produced the best results. H₂/CO mole ratio was adjusted by setting specific experimental parameters of the latter. CO₂ free synthesis gas was produced at higher H₂O and CH₄ flow rates, i.e. 0.8 mmol/h and higher power, i.e. 100 W. CO₂ and CO free H₂ was produced at 0.3 and 0.6 mmol/h flow rates of H₂O and CH₄, respectively, and 50 W.

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1. Introduction

Methane is a major component of natural gas and is mainly used as fuel for industrial and residential heating. It is produced much more than it is required, so any attempt to convert it into higher hydrocarbons, which in turn can be transported in the liquid phase, may be advantageous. Methane is also utilized in producing synthesis gas that could be converted into liquid hydrocarbons and other chemical products. The indirect methods to transform it have the disadvantages of long processing time and high costs. This is due to the fact that the direct coupling of methane to C_n hydrocarbons is thermodynamically unfavourable because methane molecules have higher stability.

At present, only the steam reforming process is industrially used to produce synthesis gas from methane. However, it reports some problems. Since the process is

highly endothermic, a high operating temperature, usually higher than 1073 K, is required. Therefore, developing new techniques and processes of direct conversion of methane to higher hydrocarbons and synthesis gas became a challenging research subject.

It is known that plasmas can effectively activate methane molecules. Particularly, low-temperature non-equilibrium plasmas can improve the selectivity of products, and their research became more active lately. Conversion of methane, both pure and mixed with several gases, with and without catalysts, has been performed by means of several techniques, namely microwave (MW) plasmas [1–5], corona discharges [6–10], high voltage in microchannel plates [11,12], DC pulsed discharges [13], dielectric barrier discharges [14], and arc plasmas [15]. Pressures ranged from 1 Pa (0.0075 Torr) to 0.13 MPa (1.28 atm). Conversion of methane to higher hydrocarbons and its reforming to synthesis gas showed diverse values depending upon the conditions of the plasmas. Particularly, in the reforming experiments methane has been injected into the discharges mixed with one or more other gases.

This paper gives account of the first reported studies related to the activation of CH₄/H₂ mixtures by means of

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capacitive-coupled radio-frequency (rf) plasmas, following a response surface methodology, (RSM) [16–19]. The same rf system was employed to study the reforming of methane with plasmas of O₂, CO₂ and steam, respectively. CH₄ was injected downstream, and the effects of the gas pressure, rf power, and the position at which injection of methane took place were investigated.

2. Experimental

A schematic view of the experimental apparatus is depicted in Fig. 1(A). It is a modification of systems previously employed to oxidize liquid hydrocarbons and diesel fuels [20,21]. The reactor is a double-walled cylindrical glass vessel of approximately 2.5 cm inner diameter. An rf system is employed to produce the plasma; it uses a Branson IPC 100 generator that works at 13.4 MHz and supplies a power up to 100 W. To get an efficient coupling between the generator and the electric discharge, a matching box is used to connect the former to a copper coil. The latter is positioned externally around the reactor. The discharge is produced at this point through the gas injected from the top. An internal conical tube with maximum diameter of 1.5 cm carries the plasma downstream. At the end of this cone there are two options: in the case of non-oxidative coupling of methane, i.e. activation of CH₄/H₂, the mixture of gaseous products is drawn by the vacuum pump and a sample of it is collected in the trap for later analysis. In the reforming experiments, an additional gas inlet is connected perpendicular to the reactor, right at the end of the internal tube, as shown in Fig. 1(B), with the objective of injecting methane. At this point, the plasma of O₂, CO₂, and steam reacts with methane and the products are collected as before.

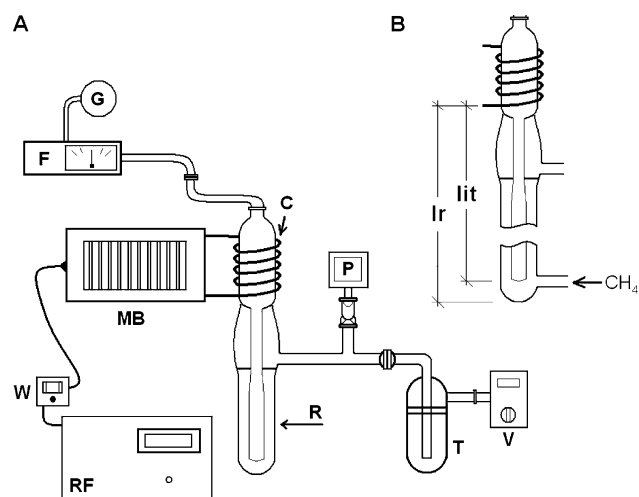


Fig. 1. Diagram of the experimental assembly. (A) G: gas or water reservoir; F: flow meter; C: copper coil; MB: matching box; W: power meter; RF: power supply; R: reactor; P: pressure meter; T: trap; V: vacuum pump. (B) lr: length of reactor; lit: length of internal tube.

The gas flow rate is measured with a 247 B-MKS flow meter and the pressure is monitored with a Leybold-Heraeus TM111 thermotron. The products of the reactions are identified and quantified by means of gas chromatography. A Perkin Elmer Auto System XL chromatograph, equipped with a thermal conductivity detector (TCD), is employed. For the direct conversion of methane, an RT alumina column is used and N₂ is the carrier gas. For the reactions with O₂, CO₂, and H₂O plasmas, a *carbosieve* S_{II} column is employed and argon is the carrier gas.

3. Results and discussion

3.1. Activation of methane/hydrogen

Non-oxidative coupling of methane was studied by injecting mixtures of CH₄ and H₂ into the reactor, and by varying rf power, total pressure, and CH₄/H₂ mole ratio.

RSM [16–19] was adopted to obtain an approximate mapping of response surface and the attainment of the most acceptable operating conditions. A Box-Wilson central composite design was used. It contains an imbedded two levels factorial or fractional-factorial design with centre points, that is augmented with a group of ‘star points’ that allows estimation of curvature. The three factors studied were rf power (watts), system pressure (mbar), and methane/hydrogen mole ratio. The reactor was not changed through this part of the study. The central composite design used an axial spacing of $\alpha = \pm 1.68$, which approximates orthogonality and rotatability [16,19]. Nine centre points were used for a total of 23 design points. The actual numerical measures of the variables ξ_i were coded. The current region of interest for ξ_i was defined as $\xi_{i,0} \pm s_i$, where $\xi_{i,0}$ is the centre of the region. Then, it would be convenient to define an equivalent working variable x_i :

$$x_i = \frac{\xi_i - \xi_{i,0}}{s_i}, \quad (1)$$

where the coded quantities x_i are simply convenient linear transformations of the original ξ_i , and expressions containing x_i can always be readily rewritten in terms of ξ_i .

Actual and coded values of parameters and conversion of methane are given in Table 1. Conversion is the percentage of methane that has been transformed into other compounds. Coded values, x_1 , x_2 and x_3 for power, pressure, and CH₄/H₂ mole ratio, respectively, are defined by Eq. (1).

To approximate the response surface, a second degree polynomial model for an expected response, $E(y)$, in

Table 1
Results from the composite design for methane conversion (y)

Trial	Actual levels			Coded levels			Response	
	Power (W)	Pressure (mbar)	CH ₄ /H ₂ ratio	x_1	x_2	x_3	y (%)	
1	20	0.07	1/3	-1	-1	-1	24.5	Cube points
2	80	0.07	1/3	1	-1	-1	25.9	
3	20	0.07	1/2	-1	1	-1	46.1	
4	80	0.07	1/2	1	1	-1	46.4	
5	20	0.13	1/3	-1	-1	1	6.9	
6	80	0.13	1/3	1	-1	1	16.5	
7	20	0.13	1/2	-1	1	1	36.6	
8	80	0.13	1/2	1	1	1	39.0	
9	0	0.10	2/5	-1.7	0	0	0	Star points
10	100	0.10	2/5	1.7	0	0	30.6	
11	50	0.10	1/4	0	-1.7	0	26.8	
12	50	0.10	3/5	0	1.7	0	37.8	
13	50	0.045	2/5	0	0	-1.7	35.3	
14	50	0.20	2/5	0	0	1.7	23.9	
15	50	0.10	2/5	0	0	0	27.7	Centre points
16	50	0.10	2/5	0	0	0	31.2	
17	50	0.10	2/5	0	0	0	30.5	
18	50	0.10	2/5	0	0	0	30.5	
19	50	0.10	2/5	0	0	0	32.0	
20	50	0.10	2/5	0	0	0	30.6	
21	50	0.10	2/5	0	0	0	35.2	
22	50	0.10	2/5	0	0	0	31.1	
23	50	0.10	2/5	0	0	0	30.7	

the coded inputs x_1 , x_2 , and x_3 was used:

$$E(y) = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{33}x_3^2 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3, \quad (2)$$

where β_i 's are the first-order coefficients, β_{ii} 's, are pure quadratic coefficients, and β_{ij} 's are mixed second-order coefficients. This model was least squares fitted to the data and a significance level of $\alpha=0.10$ was used to test if estimated coefficients were significantly different from zero. The significant coefficients were re-estimated for the final approximating function. A lack of fit test was run to assure that the second-order model adequately approximates the true surface. The analysis of variance for this corrected model is shown in Table 2. The final prediction equation was:

$$y = 31.3 + 11.6x_1 - 4.6x_2 - 3.3x_1^2. \quad (3)$$

Table 2
Analysis of variance including lack of fit test for methane conversion

Source	Sum of squares	Degrees of freedom	Mean square	F-ratio	P-value
x_1 (Power)	1825.76	1825.76	266.41	0.00	
x_2 (Pressure)	291.76	1	291.76	42.57	0.0000
x_1x_1	171.63	1	171.63	25.04	0.0002
Lack-of-fit	98.20	5	19.64	2.87	0.0550
Pure error	95.94	14	6.85		
Total (corr.)	2483.30	22			

R-squared =92.18%. Standard error of estimation=2.62.

Both the fitted contour levels of conversion at the bottom and the associated surface at the top, plotted in the space of rf power and pressure (x_1 and x_2), are shown in Fig. 2. The system represents an oblique 'Rising Ridge' or 'Hillside' with conversion increasing as power is progressively increased and pressure is simultaneously reduced. The same trend is observed at the bottom, with the darkest zone representing the lowest conversion and the clearest indicating the highest. The negative quadratic term in x_1 seems to be responsible for the flattening out of the surface at high rf power. A competitive reaction, like carbon formation, could be the answer for this behaviour. Another explanation could be the fact that, at high rf power, CH₄ concentration is too low to be activated effectively because conversion is high.

Selectivity for C_n hydrocarbons and methane conversion, for 23 trials, are given in Table 3. Selectivity is the percentage of each compound among the products.

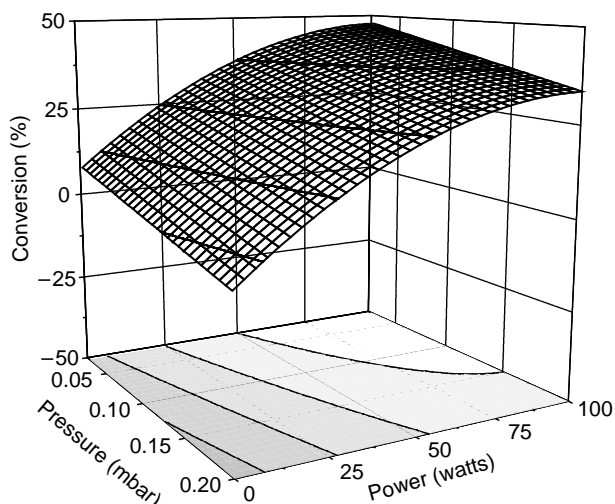


Fig. 2. Fitted contour levels of CH₄ conversion and associated surface versus rf power and pressure.

The highest CH₄ conversion (46.4%) was obtained at a power of 100 W, total pressure of 0.07 mbar, and CH₄/H₂ ratio of 1/2. C₂ are ethane (45.2%) and ethylene (11.9%); C₃ are propane (3.3%) and propylene (3.6%); C₄ are *n*-butane/isobutane (35.1%), *trans*-2-butene (0.3%), 1-butene (0.2%), isobutylene (0.2%), and *cis*-2-butene (0.2%). Products distribution for each C_{*n*} was dependent on the plasma parameters. For a given power, the highest conversion was obtained at the lowest pressure. This indicates that, when small amounts of CH₄ and H₂ molecules are injected in the plasma, they can be more effectively dissociated into

Table 3
Selectivity of different C_{*n*} hydrocarbons from methane coupling

Trial	Methane conversion (%)	C ₂ selectivity (%)	C ₃ selectivity (%)	C ₄ selectivity (%)
1	24.5	72.2	6.5	21.2
2	25.9	73.0	6.2	20.9
3	46.1	57.1	6.9	36.0
4	46.4	56.7	6.9	36.4
5	6.9	95.7	2.9	1.4
6	16.5	82.4	5.5	12.1
7	36.6	62.8	6.6	30.6
8	39.0	61.5	6.4	12.5
9	0.0	0.0	0.0	0.0
10	30.6	66.7	5.9	27.4
11	26.8	73.1	4.5	22.4
12	37.8	64.0	5.8	30.2
13	35.3	63.7	7.1	29.2
14	23.9	74.1	4.6	21.3
15	27.7	72.6	5.4	22.0
16	31.2	67.6	5.8	26.6
17	30.5	65.9	5.2	28.9
18	30.5	66.2	5.3	28.5
19	32.0	67.8	6.9	25.3
20	30.6	68.6	6.2	25.2
21	35.2	64.8	6.2	29.0
22	31.1	65.3	7.1	27.6
23	30.7	68.4	6.2	25.4

radicals which, in turn, react downstream to produce higher hydrocarbons. Power was the factor with the strongest effect on the coupling reactions. This was noticeable in Eq. (3) where power (x_1) had the highest coefficient, namely 11.6. This means that higher power applied to the plasma increases the energy of electrons, thus augmenting the production of reactive radicals in the reactor, namely H, CH₃, CH₂ and CH. CH₄/H₂ mole ratio had the lowest effect, except for the fact that experiments with ratios higher than 1/2 produced increasing amounts of black carbon and polymeric material in the reactor. These by-products were also observed when power was at the highest values. This result can be related to the negative coefficient of the second power of x_1 in Eq. (3).

In agreement with previous works, selectivity of C₂ was the highest, C₄ being second. The latter was higher than that of C₃ by factors ranging from 3.3 to 5.3. It may be that couples of CH_{*n*} preferentially react to produce C₂ molecules and part of these undergo further transformation C₂+C₂=C₄. There is an observation in Table 3 that supports this hypothesis; experiments with the lowest methane conversion, namely 5, 6, 1, 2, 9 and 14, exhibit the highest C₂ selectivity.

Equations similar to Eq. (3) were obtained for the selectivity, z , of each of the C₂, C₃, and C₄ hydrocarbons, respectively,

$$z_{C2} = 21.1 + 6.1x_1 - 2.2x_2 - 2.6x_1^2, \quad (4)$$

$$z_{C3} = 1.79 + 0.77x_1 - 0.44x_2, \quad (5)$$

$$z_{C4} = 8.1 + 4.7x_1 - 1.9x_2. \quad (6)$$

The effect of the quadratic term in x_1 , i.e. rf power, was meaningful only for C₂, in agreement with the observation for conversion of methane in Eq. (3), thus confirming the comment on black carbon formation as a negative feature.

To validate the model previously described, two new replicated experiments with a set of variables different from those reported in Tables 1 and 3 were performed. Power, pressure, and CH₄/H₂ mole ratio were 100 W, 0.07 mbar, and 1/2, coded values being 1.6818, -1, and 1, respectively. The resulting conversions differ from the estimates, predicted by using Eqs. (3)–(6), by about 5%. From these results the adequacy of the model is immediately obvious. This important result means that a particular mixture of products could be obtained by adjusting the experimental conditions.

Most of the previous works on methane coupling by plasmas have been performed with techniques that employ electrodes. Due to the fact that CH₄ makes contact with them, black carbon and tar are produced under any conditions. That did not happen with this study with rf. Those by-products were not observed in most of the runs, particularly those with the best results of conversion and higher hydrocarbons production.

3.2. Reforming of methane

With the aim of studying their effect on the composition of the products, two different distances from the external copper coil to the position where methane is injected and, hence, two lengths of the reactor were experimented, as shown in Fig. 1(B). They were 20 and 22.5 cm (short reactor), and 31 and 33.5 cm (long reactor).

3.2.1. CO₂ plasma

A search was done in order to find out the CO₂ and CH₄ pressures for best conversion. They were 0.08 and 0.2 mbar, respectively, and were constant for the rest of the study. Flow rates were 0.24 mmol/h for CO₂ and 0.6 mmol/h for CH₄. The results obtained by varying rf power with the short and long reactors are given in Table 4. In both reactors the amount of H₂ and CO increased with the power but the H₂/CO mole ratio was low, even lower with the long reactor. In this case, the amount of CO₂ in the final mixture was higher. This indicates that more of the active species produced by the electron–CO₂ collisions, namely CO molecule and O atom, recombine to produce CO₂ before reacting with methane. No liquid sample was collected at the N₂(l) cooled trap.

3.2.2. O₂ plasma

Similarly to the case of CO₂, the best O₂ and CH₄ pressures were determined, they being 0.1 and 0.2 mbar, respectively. Flow rates were 0.3 mmol/h for CO₂ and 0.6 mmol/h for CH₄. Attention was paid to avoid that CH₄ went upstream the reactor towards the position of the external coil because this would produce formation of polymers and black carbon. Ozone formation through the reaction



was avoided by keeping the oxygen pressure as low as possible. M symbolizes other particles in the plasma.

Results obtained by varying rf power with the short and long reactors are given in Tables 5. In both reactors, the amount of H₂ and CO increased by increasing rf power and H₂/CO mole ratios were, at least, five times higher than those obtained with the CO₂ plasmas. This is in agreement with the fact that CO is a primary product of carbon dioxide

Table 4

Product distribution (mol%) for the reaction of CO₂ plasmas with CH₄ in the short and long reactors

Products	30W reactor		60W reactor		90W reactor	
	Short	Long	Short	Long	Short	Long
H ₂	0.8	0.14	1.6	1.1	1.9	1.4
CO	3.7	2.4	7.2	6.0	9.4	6.8
CH ₄	67.1	66.2	64.3	62.9	63.5	62.9
CO ₂	28.4	31.3	26.9	30.0	25.2	28.9
H ₂ /CO	0.22	0.06	0.22	0.18	0.20	0.21

Table 5

Product distribution (mol%) for the reaction of O₂ plasmas with CH₄ in the short and long reactors

Products	30W reactor		60W reactor		90W reactor	
	Short	Long	Short	Long	Short	Long
H ₂	1.7	–	2.9	2.4	5.8	3.0
CO	1.4	–	2.7	2.3	5.4	3.0
CH ₄	95.9	100	93.8	95.3	87.4	94.6
CO ₂	–	–	0.6	–	1.4	–
H ₂ /CO	1.21	–	1.07	1.04	1.07	1.25

dissociation. Liquid products were observed with the oxygen plasmas, namely water and formic acid with the short reactor, and only water with the long one. All these results can be associated to the active species present in the oxygen plasma. It has been determined that, under the conditions of this study, O(³P) is the most abundant one [21,22]. When more power is applied to the discharge more energetic electrons will be available, and more oxygen molecules will be dissociated into oxygen atoms which, in turn, will produce more reactions. Due to the longer path before reaching the methane molecules in the long reactor, oxygen atoms have more probability of recombining themselves in this case, in the presence of a third body (M)



The absence of hydrogen and CO at 30 W and CO₂ at any power in the long reactor confirms the preceding observations and suggests that conditions of oxygen plasmas can be optimized in order to obtain CO₂ free synthesis gas.

3.2.3. Steam plasma

The most interesting results were obtained with steam plasmas. Previous to the reactions, optical emission spectroscopy was employed to study the active species in the plasma. The radiation was focalized, by means of a 10-cm focal-length convergent quartz lens, on the entrance slit of a 0.5-m Czerny–Turner monochromator equipped with a 1276 lines/mm diffraction grating. The emission signal was detected by a Hamamatsu R955 photomultiplier that fed a SR-250 Boxcar data collector, Stanford Research Instruments, and was finally plotted on a Cole Parmer recorder. Steam flow rate was varied in order to observe its effect on the intensity of three particular signals: the H_β line, located at 486.5 nm [23]; the OH band situated at 306.8 nm, corresponding to the $v'=0 \rightarrow v''=0$ transition of the A²Σ⁺ – X²Π_i system [24]; and the O I lines at 844.6 and 844.7 nm, corresponding to the 3p ³P → 3s ³S transition [23].

Behaviours of the identified species in the plasma are shown in Fig. 3 for different flow rates of steam and rf power of 100 W. In recording the optical emission signal for each species, the amplification of the photomultiplier had to be adjusted according to the intensity of the respective transition. Hence, each curve only shows

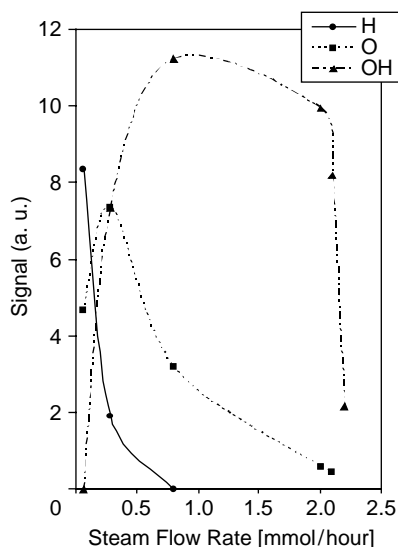
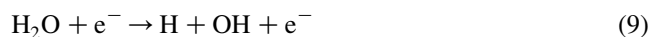


Fig. 3. Relative intensities of H, O and OH signals in the plasma as a function of steam flow rate.

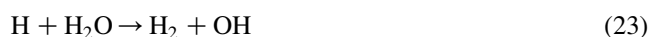
the relative population of a particular species. The hydrogen atom showed an expected tendency [25], that is, for low flow rates the energy of the discharge is enough to dissociate a relatively high number of water molecules; however, when the flow rate is increased, the recombination rate of H radicals to produce hydrogen molecules progressively equals their production. The oxygen atoms density showed a similar behaviour to that of H, as expected from a previous work with a high voltage oxygen plasma [26]. In the case being analyzed, the maximum signal of O I has been observed at about 0.3 mmol/h. Finally, the diatomic species OH showed a drastic density increase starting from ca. 0.1 mmol/h, reaching a wide range of steam flow rate for maximum production and, then, decreasing after 2 mmol/h.

The analysis of Fig. 3 led us to find out not only the appropriate flow rates to carry out specific reactions between the water plasma and methane but also it was possible to determine the chemical mechanisms involved in the plasma



Based on this sequence of reactions it is possible to explain the characteristic trends of the different species in the plasma, as shown in Fig. 3. That is the case for

the maximum value of the atomic hydrogen concentration at low flow rates, which is generated through four different sources. This means that hydrogen atoms are the main contributing agents to the system entropy and their recombination is hence possible and higher than those of other species when the flow rate is increased



W is the wall of the reactor system.

Furthermore, H exhibits recombination with atomic oxygen and water to produce OH. This may be an explanation to the maximum shown by the latter throughout a wide range of higher steam flow rate.

In order to study their effects on the production of synthesis gas and CO free H_2 , two different steam flow rates were employed to produce the plasma for reacting with methane, namely 0.3 and 0.8 mmol/h. The appropriate flow rate of CH_4 was found out in each case by using the following criteria: if it was too low there was not enough reaction; if it was too high methane entered the internal tube of the reactor thus producing black carbon and polymers. The values of 0.6 and 0.8 mmol/h were determined, respectively.

Table 6
Product distribution (mol%) for the reaction of steam plasmas with CH_4 in the short and long reactors

$F_{\text{H}_2\text{O}}$ (mmol/h)	F_{CH_4} (mmol/h)	Power (W)	H_2	CO	CH_4	H_2/CO
<i>Short reactor</i>						
0.3	0.6	50	59.2	4.9	35.9	12.1
0.3	0.6	100	66.0	14.4	19.6	4.6
0.8	0.8	50	15.5	1.9	82.6	8.1
0.8	0.8	100	21.1	7.3	71.6	2.9
<i>Long reactor</i>						
0.3	0.6	50	46.7	–	53.3	–
0.3	0.6	100	74.2	8.4	17.4	8.8
0.8	0.8	50	12.1	0.8	87.1	15.9
0.8	0.8	100	11.6	1.1	87.3	11.0

CO_2 was not detected among the products.

Results are presented in Table 6. In agreement with the CO₂ and O₂ plasmas, methane conversion increased with rf power but, contrarily to them, the change in the H₂/CO mole ratio was meaningful. At 50 W the production of H₂ was favoured. Probably, at 100 W the formation of oxygenated compounds are favoured due to the higher production of oxygen atoms through reactions (9)–(14).

Better results were obtained at lower flow rates, in terms of both H₂ amounts and H₂/CO mole ratios. CO₂ free mixture of H₂/CO at a mole ratio of 2.9 was produced at higher H₂O and CH₄ flow rates, i.e. 0.8 mmol/h, and 100 W. That was the maximum power delivered by the rf generator. According to the results in Table 6, a mole ratio of 2.0 could be obtained at a power no much greater than 100 W.

CO₂ and CO free H₂ was produced at 0.3 and 0.6 mmol/h flow rates of H₂O and CH₄, respectively, and 50 W. That confirms the higher populations of ¹H and O observed at 0.3 mmol/h of water compared to those at 0.8 mmol/h. Such a result had not been reported in similar plasma studies published recently [1,13–15].

It is interesting to note that the high amounts of OH at medium to high water flow rates did not have effects on the results, confirming the low reactivity of this species under the conditions of the experiments [20].

4. Conclusions

Coupling reactions of CH₄–H₂ were accomplished by means of rf discharges for the first time, reaching conversions similar to those of previous works with other techniques. Values can be increased by increasing rf power and pressure of the starting gases. A response surface methodology allowed a modelling of the experiments, showing that it is adequate to describe the observed data and to predict results for random experiments. Methane conversion was described by a second degree polynomial containing the parameters of the plasma.

Reforming of methane was performed by means of rf discharges through CO₂, O₂, and steam separately, which reacted with methane injected downstream in the reactor. Oxygen plasmas were the most oxidant whereas the best results were obtained with steam plasmas. H₂/CO mole ratio was adjusted by setting specific experimental parameters of the latter. CO₂-free synthesis gas was produced at high H₂O and CH₄ flow rates and high power. At certain conditions H₂/CO mole ratios up to 16 were obtained. CO₂ and CO free H₂ was produced at low flow rates of H₂O and CH₄ and 50 W. This result could be interesting in the field of producing hydrogen and fuel cells.

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