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Selectivity Control in a Microwave Surface-Wave Plasma Reactor for Hydrocarbon Conversion

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Abstract. Drastic changes in the selectivity towards different products have been found in the transformation of n-hexane in a microwave surface-wave plasma reactor. Either ethylene or hydrogen can be obtained with a high selectivity by selecting some reaction/plasma parameters such as applied microwave power, hydrocarbon flow rate or feed position. These results have been related to alternative plasma-chemical routes revealing the high versatility of surface-wave sustained discharges for the fine control of the hydrocarbon reactivity and so opening the door to new selective plasma-chemical processes.

Introduction

In the last years, the use of plasmas in hydrocarbon reforming applications such as hydrogen and synthesis gas production, growth of carbon nanotubes, deposition of diamond-like carbon films, conversion of natural gas or treatments of effluents containing volatile organic compounds, has remarkably augmented. Among other facts, the intense search in the last decade for new technologies facilitating the conversion of methane and light naphtha into valuable products, such as higher hydrocarbons, synthesis gas and oxygen-containing compounds, has contributed to this increase. Also, the effective utilization of natural gas and biogas to provide alternative petrochemical feedstocks, for example the oxygen-free conversion of methane into aromatics, and the CO_x-free hydrogen production for fuel cells are considered highly beneficial.^[1]

In recent years, a huge interest for fuel cell development has arisen as a good alternative to fuel (diesel, gasoline) based combustion engines in terms of efficiency and environmental impact.^[2] However, the technology based on hydrogen has significant drawbacks due to its storage properties (low density and high flammability risk). The development of onboard systems capable of converting liquid hydrocarbon fuels, such as gasoline, into a stream of H₂-rich gas and carbon would make possible to power internal combustion engine vehicles using standard fuels with H₂.^[3] Moreover, the capture and storage of carbon onboard the vehicle could help to mitigate climate change.

The preparation of carbon thin films, which are of great interest because of their physical and chemical properties (e.g., good hardness, high thermal conductivity, good electric resistivity...), by decomposition of hydrocarbons has also played an important role in the development of plasma assisted hydrocarbon reforming.^[4,5]

Plasma technology is very promising for hydrocarbon conversion.^[6,7] Plasma processes combine high chemicals reactivity with low operational cost, and appear as an interesting

alternative to the conventional methods of hydrocarbon reforming such as catalytic autothermal or dry reforming.^[7-9]

Historically, first plasma assisted reformers were thermal ones (e.g. direct current plasma torch). In those reactors, chemical reactions were enhanced because of the presence of very reactive species, such as ions and electrons, in a very hot medium. However, the thermal-plasma application in hydrocarbon reforming is not very effective because most of the energy is used in heating particles. On the contrary, non-thermal plasmas are considered as a very promising technology due to their non-equilibrium properties: low power requirement and its capacity to induce physical and chemical reactions within gases at relatively low temperatures.^[10] It is the high electron temperature what determines the unusual chemistry of non-thermal plasmas.^[2] Thus, the collisions of highly energetic electrons with neutral species produce ionization, fragmentation of molecules, and electronic, vibrational, and rotational excitation of the neutral gas. The electron induced collisions can produce free radicals from parent molecules in multi-step physical and chemical processes, and these free radicals react with and decompose hydrocarbons.^[10]

Non-thermal plasmas comprise very different types including glow discharge, corona discharge, silent discharge, DBD, radio frequency discharge and microwave discharge. In the past few years, a significant amount of theoretical and experimental works has been conducted on the behavior of microwave induced plasmas (MIPs) because their use in a great number of scientific and technological fields has grown significantly. Nowadays, these discharges are being employed in elemental analysis, surface treatment, lighting, destruction of contaminant gases, or sterilization, among other applications.^[11] Among microwave induced plasmas, surface-wave sustained discharges (SWDs) in dielectric tubes are especially interesting. Their unique features, such as high flexibility, ease of handling or their ability to be generated under a broad range of experimental conditions, are responsible for the attention that SWDs have attracted in the last decades.^[12] Moreover, SWD columns are not confined

within the microwave power coupling device, having dimensions that can be easily changed and controlled by applying different microwave powers. This last characteristic, that other kinds of MIPs do not possess,^[11] could be very useful since it allows to optimize the design of the plasma reactor for each application. Hydrocarbon reforming is one application of microwave plasmas that in the last years has gained much interest because of the wide range of possibilities that it offers in the different abovementioned applications.^[13-18]

In general, the deficiency of most hydrocarbon conversion methods based on the use of non-thermal plasma lies in their low selectivity. In a plasma, miscellaneous active species are generated, i.e., free radicals, ions and excited molecules, that become the precursors for a number of chain reactions with the formation of different final products. For this reason, in the last years some researchers have concentrated their investigations on the issue of the selectivity. Thus, Schmidt-Szalowski et al.^[9,19] have proposed a hybrid plasma-catalytic system to improve the selectivity towards different final products (ethane, ethylene, acetylene, hydrogen, carbon monoxide, carbon and methanol, among others) in the conversion of methane, dependent on discharge conditions, particularly of the input-energy density. Also, Ghorbanzadeh et al.^[20,21] have used a non-thermal pulsed plasma (glow discharge type) reactor for methane conversion too which has allowed a very good control over the selectivity by changing the pulse repetition rate.

Herein we report the drastic changes in selectivity, particularly towards hydrogen and ethylene with both chemicals being of outstanding importance for the chemical industry, which happen in a microwave surface-wave plasma reactor after the introduction of n-hexane, which was selected as a model compound for light naphtha. The influence of several operating conditions has been found to be decisive in the plasma chemistry which finally determines the reaction products.

Experimental Part

Plasma reactor

The microwave plasma was generated in a quartz tube reactor of 12 and 16 mm of inner and outer diameter, respectively (**Figure 1**). A surfaguide device was employed as a launcher of surface-waves that mainly propagate along the dielectric-plasma interface creating and sustaining a plasma column inside the tube.^[22] In this way, microwave powers (coming from a SAIREM GMP 20 KED 2.45 GHz generator) ranging from 100 to 400 W were coupled to the plasma and a vacuum pump was used to maintain a pressure of about 10 Torr inside the tube. The movable plunger and stubs permitted the impedance matching so that the best energy coupling could be achieved, making the power reflected back to the generator (P_r) negligible (< 5%). Argon flow rate was set at $100 \text{ ml}\cdot\text{min}^{-1}$, and was adjusted with a calibrated mass flow controller.

Because the injection of liquids in SWDs provokes the extinction of the plasma, a system of introduction of liquid samples based on the previous evaporation of the liquid with the assistance of an auxiliary gas (Controlled Evaporator Mixer, Bronkhorst) was employed. Argon was chosen as a carrier gas at a flow rate of $25 \text{ ml}\cdot\text{min}^{-1}$. The plasma reactor was designed in such a way that the hydrocarbon could be introduced at different axial positions (z , where the position $z = 0$ was set at the end of the plasma column) corresponding to both the plasma region itself (z negatives) and the afterglow zone (z positives, beyond the end of the plasma column). Remote processes (those taking place in the afterglow) would be expected to be mainly controlled by neutral chemistry, in contrast with those occurring in the plasma column where the microwave energy density is higher, and so electrons might play a significant role in the plasma kinetics.

Analysis techniques

Optical Emission Spectroscopy (OES) techniques were employed in order to gain knowledge about the hydrocarbon cleavage process inside the plasma and afterglow. OES is a non-invasive technique of very simple experimental implementation (since only requires a diagnostic port providing a line-of-sight through the plasma), that does not affect the plasma and offers the possibility of observing the plasma in real-time. On the other hand, the combination of OES techniques with gas chromatography and mass spectrometry has permitted to get a better understanding of the chemical processes that take place in the plasma and afterglow leading to the production of hydrogen and other hydrocarbons as well as to the deposition of carbon films.

The emission spectra of the plasma and afterglow were analyzed by using an AvaSpec Multichannel Fiber Optic Spectrometer, configured with three 75 mm focal length spectrometer (Czerny–Turner type) channels, all consisting of 2 048 pixel CCD detectors, holographic diffraction gratings of 1 200 grooves/mm, and 10 μm slit width (spectral resolution in 0.1–0.2 nm range). Emission from the plasma and afterglow were side-on collected at different axial position of the plasma column through three optical fibers every one connected to their corresponding spectrometer channel. Spectra recorded permitted us both to gain information about the different species existing in the different regions plasma and to estimate the gas temperature from the theoretical simulations of CN (violet system at 388 nm) spectra and their comparisons to the experimental ones. For this purpose, LIFBASE software developed by Luque and Crosley^[23] was employed.

The identification and the analysis of the reaction products were carried out by using a gas chromatograph (Varian 450, equipped with both FID and TCD detectors) and a quadrupole mass spectrometer (OmniStar from Pfeiffer Vacuum) connected on line to the reactor tube. The separation of all compounds was accomplished in a CP-Porabond U capillary column (25

m × 0.32 mm i.d.) with an oven program of 50 to 150 °C at 4 °C·min⁻¹. Both mass spectrometer and gas chromatograph were previously calibrated by using standards.

The results obtained from the reaction of n-hexane were expressed as follows:

$$\text{n-Hexane conversion} = [F_o(\text{n-hexane}) - F(\text{n-hexane})]$$

$$\text{Overall n-hexane conversion (\%)} = [F_o(\text{n-hexane}) - F(\text{n-hexane})] / F_o(\text{n-hexane}) \times 10^2$$

where $F_o(\text{n-hexane})$ and $F(\text{n-hexane})$, both in mol·h⁻¹, denote the flow rates of the paraffin in the feed and the product gas, respectively, and

$$\text{Production rate} = F(\text{product})$$

where $F(\text{product})$ indicates the flow rate of each compound in the product gas (in mol·h⁻¹).

Results and Discussion

n-Hexane was transformed inside the microwave plasma reactor under different experimental conditions. As depicted in **Figure 2**, the percentage overall conversion varied in a very broad range. In general, it slightly increased as the hydrocarbon feed was placed closer to the end of the plasma column and later decreased in the afterglow. This effect was more drastic as either the n-hexane flow rate went down or the microwave power rose. In fact, at the higher flow rate, i.e. $3.92 \cdot 10^{-2}$ and particularly $5.49 \cdot 10^{-2}$ mol·h⁻¹ of n-hexane, the conversion increased steadily from the plasma region to the afterglow one.

The influence of the n-hexane flow rate and the applied microwave power on the conversion of n-hexane is depicted in **Figure 3**. As expected, the conversion of n-hexane (expressed as converted moles) increased both with the microwave power and the hydrocarbon flow rate regardless of the feed position. Interestingly, the variation against the n-hexane flow rate was quite different depending on whether the feed was introduced in the plasma ($z = -2$ cm) or the afterglow ($z = +2$ cm). In the first case, the conversion linearly increased until it reached a plateau, whereas in the second one it exponentially grew as the

flow rate rose. These results suggest different mechanisms of hydrocarbon transformation for the two regions studied.

In the plasma region, electrons (which absorb in first instance the microwave energy from the electromagnetic field)^[11] must be implied in the scission mechanisms of hydrocarbon molecules, through direct electron impacts. Nevertheless, in these argon surface-wave-sustained discharges at reduced pressures the population density of argon atomic metastable states has been found to be in the same order of the electron population density,^[24] and so argon metastable atoms could be also taking part in the microscopic processes leading to the hydrocarbon conversion. In fact, the C-H and C-C bond dissociation energies are 4.1-4.5 and 3.8 eV, respectively,^[25] whereas the excitation energy of metastable argon atoms is around 11.6 eV. Since the number of electrons and argon metastable atoms in the plasma column generated under a set of particular experimental conditions (microwave power, argon flow rate) is constant, they could only transform a maximum amount of n-hexane molecules.

On the other hand, the behavior observed in the afterglow region was totally different because the larger the hydrocarbon feed rate the higher the converted molecules of n-hexane.

Accordingly, some reactive intermediates generated by reaction between n-hexane molecules and afterglow active species should act as chain propagators. Kinetics in the afterglow is dominated by long-lived species, i.e. metastable species of long radiative lifetime or atoms in ground electronic state, through energy transfers, recombination processes and diffusion to the walls.^[26] Thus, metastable argon atoms are likely the main active species in the afterglow region of the microwave plasma utilized.

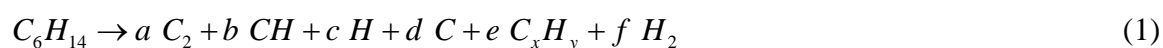
Gas (rotational) temperatures in plasma and afterglow regions, estimated from theoretical simulations best reproducing profiles of CN violet system at 388 nm by using LIFBASE software, were very similar in all the cases studied ranging from 1 300 to 1 500 K (**Figure 4**). So, the differences in reactivity between the plasma and the afterglow could not be ascribed to different plasma gas temperatures.

Interestingly, the selectivity in the transformation of n-hexane also changed very much depending on where it was introduced (**Figure 5, 6 and 7**). Thus, n-hexane fed into the plasma column at any position produced a mixture of light hydrocarbons (methane, ethylene, acetylene, and C₃ and C₄ alkenes and alkanes) and hydrogen, as well as a carbonaceous residue downstream in the afterglow region. The selectivity toward each product, i.e. its production in relation to the conversion of n-hexane, varied as a function of the flow rate and the microwave power but ethylene was usually the major compound. Its selectivity increased specifically at low hydrocarbon flow rate and high power. However, when n-hexane was introduced into the afterglow, the main products were hydrogen and concomitantly a carbon film. This tendency was especially dramatic as the n-hexane flow rate and the applied microwave power increased. In fact, by adjusting the different operational variables it was possible to obtain a high selectivity toward either ethylene or hydrogen (**Table 1**). The selectivity toward hydrogen in the afterglow was as high as 90%, similar to the values reported by Jasinski et al.^[27] for the methane reforming in a waveguide-based nozzleless cylinder-type MPS (Microwave Plasma Source) at atmospheric pressure with powers ranging from 3000 to 5000 W.

Figure 8 shows a typical optical emission spectrum recorded upon introduction of n-hexane in the plasma region ($z = -2$ cm). In general, all the optical emission spectra measured in this case at different axial positions exhibited: i) a relatively strong emission of lines of the Ar I (atomic argon) system (corresponding to radiative de-excitation of 4p and 4p' levels), of H I (atomic hydrogen) system (H_α, H_β and H_γ) and of the molecular bands of NH (3 360 Å system) and CN (violet system); and ii) a moderate emission of OH (3 060 Å system), N₂ (second positive system), CH (4 300 Å system) and C₂ (Swan system and High Pressure system) molecular bands. **Table 2** summarizes the band heads identified for each molecular band detected and their spectroscopic characteristics.^[28]

Figure 9 depicts the axial behavior of the intensity of 826.45 nm Ar I line, of H β line and of C₂ (Swan system) at 512.93 nm and of CH (4 300 Å system) at 431.42 nm band heads upon feeding of the hydrocarbon in the plasma column (z = -2 cm). The intensity of the Ar I line decreased axially whereas those corresponding to H β line, CH and C₂ band heads grew. The decrease of the density population of excited argon atoms as the distance to the microwave coupling device increases is a typical behavior of argon SWD columns.^[24] Moreover, a quenching of activated argon species upon hydrocarbon introduction was expected. The introduction of hydrocarbons is likely to quench argon metastable species which play an important role in the kinetics of this microwave plasma at reduced pressure.^[24]

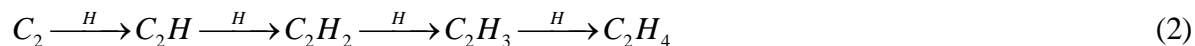
The emission of new species coming from the hydrocarbon scission (**Equation 1**), such as hydrogen atoms and C₂ and CH species, was low at positions near to the hydrocarbon feed: these species would require a residence time long enough to be efficiently excited. The increment in the excitation of these species with the axial distance (to the coupling device) was accompanied by the de-excitation of argon species.



The presence in the spectra of NH, CN, CH and C₂ species, whose intensity increased as the hydrocarbon flow rate rose, confirmed the existence of H and C atoms (as well as N atoms) in the plasma resulting from the hydrocarbon (and nitrogen, which was present as pollutant at trace level in argon main gas) dissociation. Emission spectra also showed the scant presence (or the inexistence) in the plasma of species such as H₂ or C_xH_y.

Thus, OES observations suggested that in the plasma region a complete dissociation of the hydrocarbon molecules took place in first instance through the cleavage of C-C and C-H bonds. Nonetheless, thermodynamics conditions in the plasma allowed the formation of diatomic species such as C₂ and CH. Passing through the afterglow region, these species

would be hydrogenated leading to C₂H₄ (**Equation 2**) and CH₄ whereas the recombination of H atoms would yield H₂.



This was supported by the correlation between the intensity of the C₂ band and H_β line emissions and the ethylene and hydrogen productions, respectively (**Figure 10**). Noteworthy, the amount of C₃ to C₅ hydrocarbons was rather low, which suggested that the radical intermediates generated by cleavage of C-C and/or C-H bonds from n-hexane successively would split into smaller fragments, similarly to a thermal pyrolysis mechanism (**Equation 3 to 7**).



The preferential formation of ethylene from hexane inside the column of this plasma could be explained by the well-known fact that temperatures below 1 500 K favor the production of ethylene from paraffins without the formation of acetylene.^[29] In consequence, certainly the hydrogenation of C₂ species and maybe the cracking of some n-hexane molecules would account for the production of ethylene.

Figure 11 shows the axial evolution of the intensity of 727.29 nm Ar I line, of H_β line and of C₂ (at 512 nm) and CH (at 430 nm) band heads when the hydrocarbon feed took place at the afterglow (z = +2 cm). The population density of all these species decreased in a similar way

towards the end of the reactor tube. This figure also shows that a small fraction of the hydrocarbon diffused upstream back to the plasma column where it was cleaved, being the resulting species observed by OES. For $z > +2$ cm the emission spectra did not show any excited species unless 4p argon excited atoms that were detected even at $z = +8$ cm. Based on these considerations and taking into account the high selectivity to H_2 , it could be assumed that in the afterglow active species (likely argon metastable atoms) would induce hydrogen abstraction from n-hexane. Thus, energy transfer processes between argon metastable atoms and hydrocarbon molecules could be responsible for the hydrocarbon dehydrogenation (**Equation 8**):



Similar mechanisms were proposed by Mishra et al.^[30] and C. Riccardi et al.^[31] for plasma assisted methane dehydrogenation and by Morita et al.^[32] for ethane dehydrogenation.

Moreover, the conversion profiles (see Figure 3) suggested that argon metastable atoms would have promoted the formation of some reactive intermediates in the initiation step. According to the OES results, the hydrocarbon (R_i-H) would be cleaved into an alkyl radical and hydrogen (**Equation 9**). Subsequently, both species would participate in the propagation steps (**Equation 10** and **11**) by cleavage of C-H bonds and formation of C-C and H-H bonds. Since the R_i and R_j fragments could belong to the same or different molecules the global reaction would finally yield hydrogen and a carbon residue (**Equation 12**).





Conclusion

This work has proven that it is possible to favor different reaction routes in a microwave surface-wave plasma reactor. As shown, the decomposition of a light paraffin can be preferentially conducted towards ethylene or hydrogen (free from carbon monoxide and so very suitable for use in fuel cells),^[33] depending on where the hydrocarbon feed into the reactor was performed. In addition, our investigations open up new possibilities to the development of many other radical reactions in the afterglow of these plasmas, thus expanding the application of microwave plasmas not only for chemicals production but for VOCs abatement, thin films deposition, surface treatment, etc.

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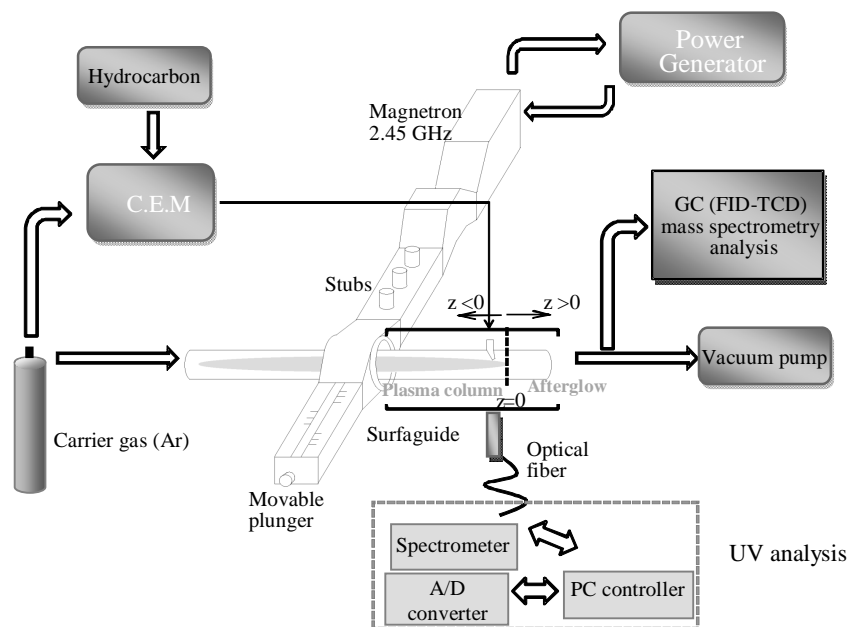


Figure 1. Experimental set-up.

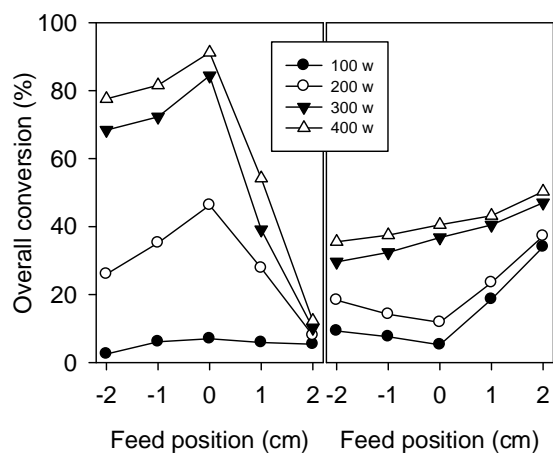


Figure 2. Overall conversion as a function of the feed position at several z for different microwave powers (n-hexane feed rates: left, $7.85 \cdot 10^{-3} \text{ mol} \cdot \text{h}^{-1}$; right, $5.49 \cdot 10^{-2} \text{ mol} \cdot \text{h}^{-1}$).

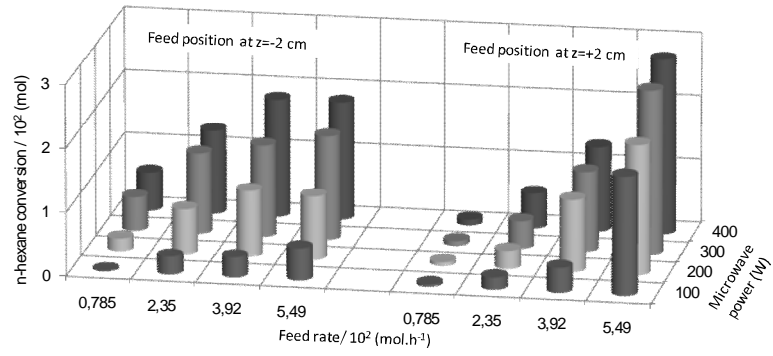


Figure 3. n-Hexane conversion as a function of microwave power and hydrocarbon feed rate, for two different hydrocarbon feed positions ($z = -2$ cm in the plasma column and $z = +2$ cm in the afterglow).

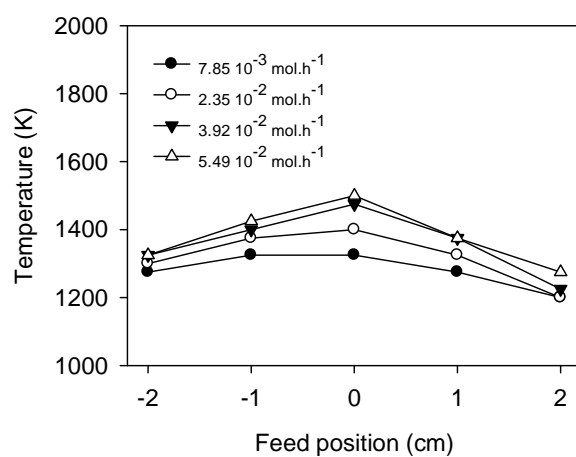


Figure 4. Rotational temperatures at 300 W estimated from theoretical simulations best reproducing profiles of CN violet system at 388 nm (measured at the feed position) by using LIFBASE software.

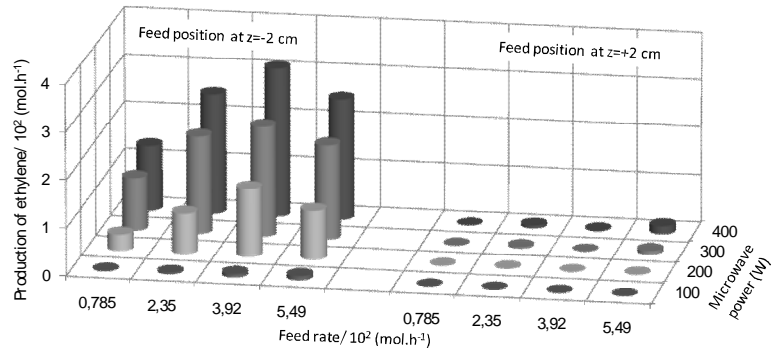


Figure 5. Production of ethylene as a function of microwave power and hydrocarbon feed rate, for two different n-hexane feed positions ($z = -2$ cm in the plasma column and $z = +2$ cm in the afterglow).

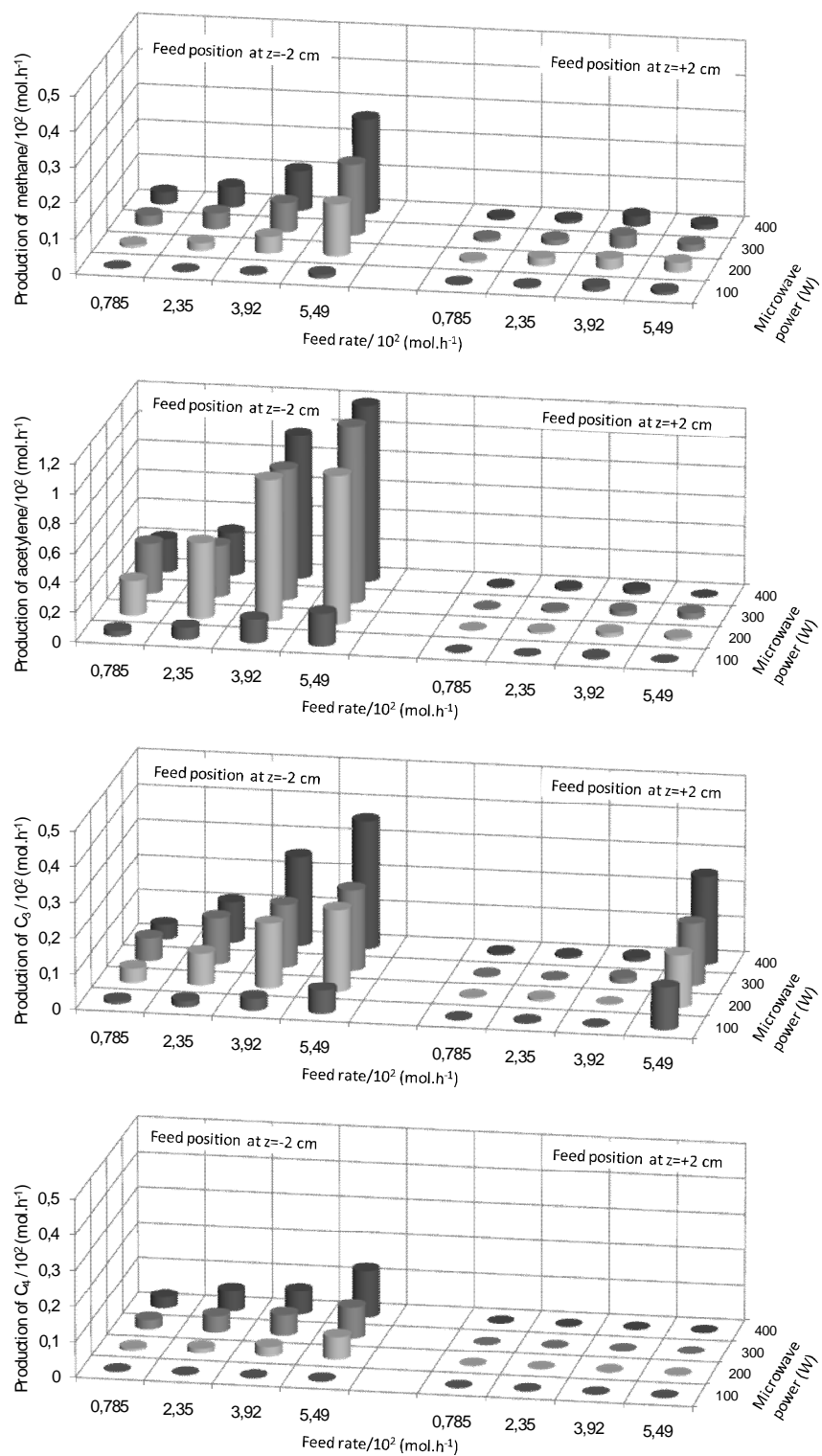


Figure 6. Production of methane, acetylene, C₃ and C₄ hydrocarbons as a function of microwave power and hydrocarbon feed rate, for two different n-hexane feed positions (z = -2 cm in the plasma column and z = + 2 cm in the afterglow).

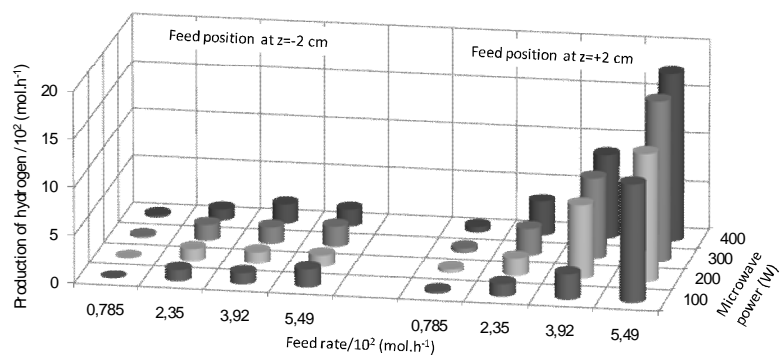


Figure 7. Production of hydrogen as a function of microwave power and hydrocarbon feed rate, for two different n-hexane feed positions ($z = -2$ cm in the plasma column and $z = +2$ cm in the afterglow).

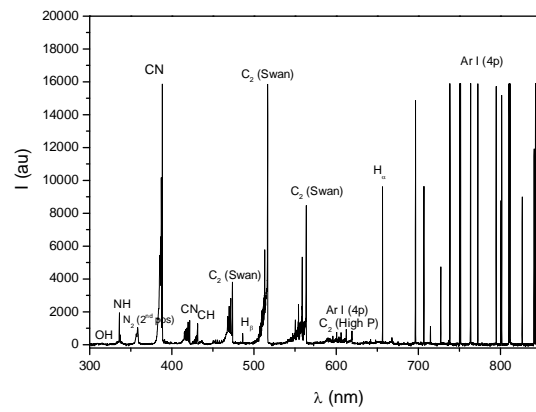


Figure 8. Characteristic OES spectra emitted by the discharge upon n-hexane feed in the plasma region ($z = - 2$ cm).

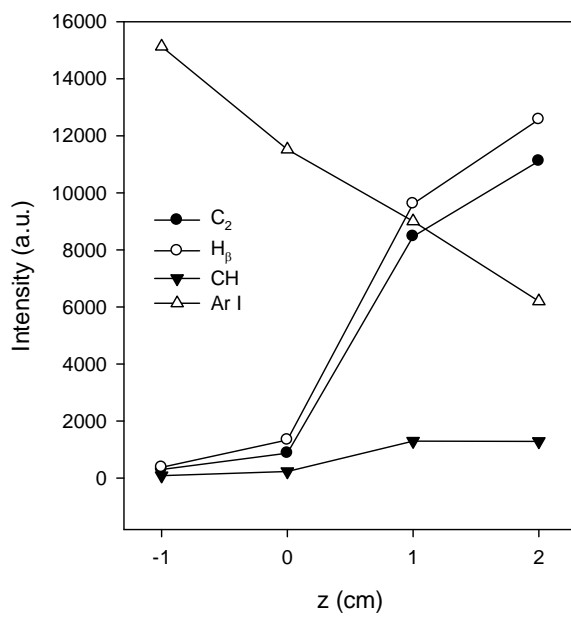


Figure 9. Typical axial evolution of OES intensities for some atomic lines (H_{β} and Ar I at 826.45 nm) and band heads (C_2 at 512.93 nm and CH at 431.42 nm) upon hydrocarbon introduction ($2.35 \text{ mol}\cdot\text{h}^{-1}$) at $z = -2 \text{ cm}$ in the plasma column at 300 W.

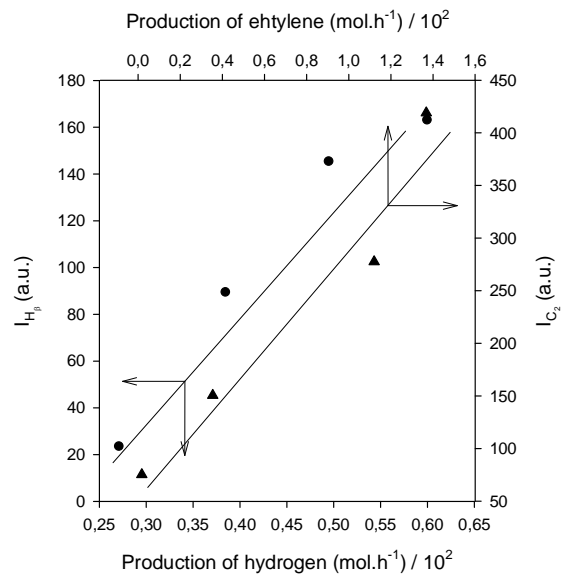


Figure 10. OES intensity of H β line vs. hydrogen production and OES intensity of C₂ band head at 512.93 nm vs. ethylene production.

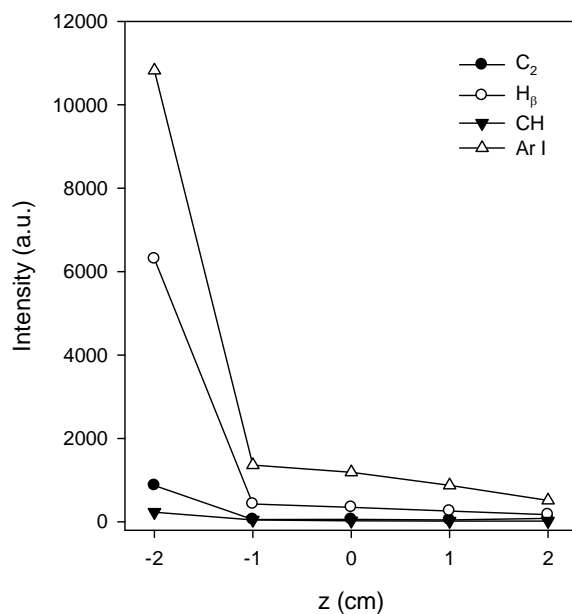


Figure 11. Typical axial evolution of OES intensities for some atomic lines (H_β and Ar I at 727.29 nm) and band heads (C₂ at 512.93 nm and CH at 431.42 nm) upon hydrocarbon introduction (2.35 mol·h⁻¹) at z = + 2 cm in the afterglow at 300 W.

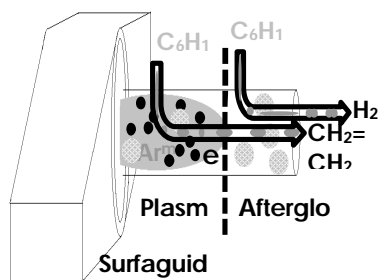


Figure for summary.

Table 1. Selected conditions for the maximum yield of products of interest according to the conditions tested in this study. The theoretical production has been calculated according to the stoichiometry in parenthesis and the selectivity as production / theoretical production x 100.

Product	Experimental conditions	Overall conversion	Production	Theoretical production	Selectivity
		(%)	(g·h ⁻¹)	(g·h ⁻¹)	(%)
H ₂	Hexane flow rate: 5.49 10 ⁻² mol·h ⁻¹ Microwave power: 400 w Feed position: afterglow (z=+2cm)	50.3	0.352	0.390 (C ₆ H ₁₄ →7H ₂ +6 C)	90.3
CH ₂ =CH ₂	Hexane flow rate: 7.85 10 ⁻³ mol·h ⁻¹ Microwave power: 400 W Feed position: column (z = -2 cm)	91.2	0.464	0.601 (C ₆ H ₁₄ →3C ₂ H ₄ +H ₂)	77.2

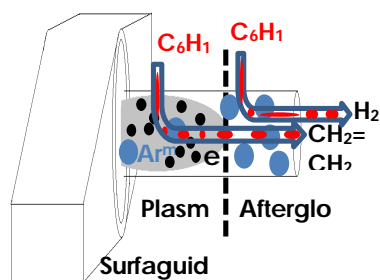
Table 2. Spectroscopic features of diatomic species observed by OES in the plasma.

Species	λ	Transition	v', v''
	nm		
OH	308.90	$A^2\Sigma^+ \rightarrow X^2\Pi$	0, 0
NH	336.01	$A^3\Pi \rightarrow X^3\Sigma^-$	0, 0
N ₂	315.93	$C^3\Pi_u \rightarrow B^3\Pi_g$	1, 0
	337.13	$C^3\Pi_u \rightarrow B^3\Pi_g$	0, 0
	353.67	$C^3\Pi_u \rightarrow B^3\Pi_g$	1, 2
	357.69	$C^3\Pi_u \rightarrow B^3\Pi_g$	0, 1
	CN	386.19	$B^2\Sigma \rightarrow X^2\Sigma$
387.14		$B^2\Sigma \rightarrow X^2\Sigma$	1, 1
388.34		$B^2\Sigma \rightarrow X^2\Sigma$	0, 0
421.60		$B^2\Sigma \rightarrow X^2\Sigma$	0, 1
CH	431.42	$A^2\Delta \rightarrow X^2\Pi$	0, 0
C ₂	469.76	$A^3\Pi_g \rightarrow X'^3\Pi_u$	3, 2
	471.52	$A^3\Pi_g \rightarrow X'^3\Pi_u$	2, 1
	473.71	$A^3\Pi_g \rightarrow X'^3\Pi_u$	1, 0
	512.93	$A^3\Pi_g \rightarrow X'^3\Pi_u$	1, 1
	516.52	$A^3\Pi_g \rightarrow X'^3\Pi_u$	0, 0
	550.19	$A^3\Pi_g \rightarrow X'^3\Pi_u$	3, 4
	554.07	$A^3\Pi_g \rightarrow X'^3\Pi_u$	2, 3
	558.55	$A^3\Pi_g \rightarrow X'^3\Pi_u$	1, 2
	563.55	$A^3\Pi_g \rightarrow X'^3\Pi_u$	0, 1
	600.49	$A^3\Pi_g \rightarrow X'^3\Pi_u$	3, 5
	605.97	$A^3\Pi_g \rightarrow X'^3\Pi_u$	2, 4
	612.21	$A^3\Pi_g \rightarrow X'^3\Pi_u$	1, 3
	619.12	$A^3\Pi_g \rightarrow X'^3\Pi_u$	0, 2

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A new argon microwave surface-wave-sustained plasma reactor can be used for n-hexane reforming. Either ethylene or hydrogen (free from carbon monoxide and so very suitable for use in fuel cells) can be obtained with a high selectivity. The plasma columns generated inside this reactor have dimensions that can be easily controlled by applying different microwave powers. This makes possible a fine selectivity control, achieved by increasing or reducing the dimensions of the plasma region against those of the afterglow one, which the hydrocarbon has to pass through before it exits from the reactor.

When the hydrocarbon is introduced in the plasma region, ethylene is the major compound in the reactor effluent while hydrogen is the main product when n-hexane is introduced into the afterglow region. Optical Emission Spectroscopy results reveal that upon n-hexane introduction in the plasma region, a complete dissociation of the hydrocarbon molecules takes place through the cleavage of C-C and C-H bonds, likely provoked by collisions with electrons and argon metastable atoms. Diatomic species such as C_2 and CH are generated in the plasma and passing through the afterglow region are hydrogenated leading to the formation of ethylene. The introduction of n-hexane in the afterglow mainly provokes its dehydrogenation induced by the afterglow active species (likely argon metastable atoms).



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