1. Introduction

The chapter deals with the chemical kinetics in the gas-phase of cold plasmas. After a section concerning cold plasmas and the modeling scheme of the chemical kinetics happening in their gas-phases, the text will focus on hydrocarbon plasma chemistry. After a general review of the chemical kinetic pattern, we discuss several features presenting applications to two main fields, carbon film deposition by radiofrequency low pressure plasmas (discussing a typical Plasma Enhanced Chemical Vapour Deposition process) and hydrogen reforming by atmospheric pressure plasmas.

As for the first topic, methane and other light hydrocarbon plasmas are of great interest in industrial applications, in particular in the chemical vapor deposition processes. Amorphous carbon and diamond-like thin films, suitable for mechanical and electronic applications can be prepared using low pressure discharges of hydrocarbon gases. The research in this field is mainly devoted to the understanding of the nature of the film growing mechanism but in spite of intense experimental and theoretical work it is not yet fully understood which species are responsible for the deposition process.

New data concerning the interaction of ions and hydrocarbon radicals allow to have a quite complete mapping of the relevant reaction rates in an Ar/CH₄ plasma by now and it is possible to investigate the effect of the chemical kinetics in such a system and eventually to identify the gaseous precursor of the chemical species incorporated in the deposited film. We have modeled the gas-phase chemistry of a typical radio frequency CH₄/Ar plasma used for the deposition of diamond and diamond-like carbon films, with the aim of understanding the effects of the chemical kinetics of argon ions and metastables.

As for the second topic, hydrogen reforming from methane is up to now the most viable source for large scale as well as localized production of hydrogen for fuel cell systems. Conventional reforming is carried out thermally in oven with oxygen and steam or using catalytic beds, but the development of more compact devices is actively pursued too. Plasma reformers based on different kind of discharges, as arcs, microwave plasmas and dielectric barrier discharges have been investigated so far. We present recent results concerning the viability of a hydrocarbon plasma reforming process to produce a hydrogen enriched gas-mixture based on atmospheric pressure discharges operating in the spark regime.
2. Plasma chemical kinetics

Plasmas are gas phase systems where a consistent fraction of molecules is ionised and free electrons move around interacting under electromagnetic forces in a collective fashion (Raizer, 1991). Considerable energy could be delivered to the charged components through their electric interactions. Part of this energy could be used also to promote chemical reactions between neutral molecules in the gas phase. Then plasmas could become interesting gas chemical reactors. The specificity of the gas and plasma dynamics makes them suitable for material processing and atomic chemistry (Lieberman, 1994). Besides a few examples, mostly in natural environment, plasmas are systems far from thermodynamic equilibrium. Then different energy content is normally found in electrons, charged and neutral components. In particular, when only electrons have energies far exceeding set temperature, plasma could be named cold, since its heat capacity is usually very low and thermal load is limited (Raizer, 1991). Chemical kinetics in such systems and their modelization are a fascinating field of applied research, crossing the borders of plasma, atomic physics and chemical engineering.

2.1 Modeling of the gas-phase evolution in cold plasmas

In a plasma reactor fed with a gas mixture several different processes are at work, as summarized in the scheme of fig.1 for the argon/methane system (Riccardi, 2001). In a cold plasma the characteristic discharge chemistry processes are mainly driven by free electrons which are by far the most energetic particles in the reactor, and include (Mc Daniel, 1993):

a. ionization reactions producing further free electrons and positive ions;
b. electronic transitions to excited energy levels responsible for the rich light emission spectra of the discharges, molecular excitations of reactive vibrational and rotational states;
c. molecular dissociation with production of highly reactive free radicals;
d. electron attachment, particularly important in electronegative gases.

The gas mixture composition in the reactor is determined by the chemical reactions between the reactive species and by the transport processes. The transport depends on the hydrodynamical flow driven by the pumping system, by the diffusion of the neutral and charged species towards reactor walls and by the surface interactions at gaseous-solid interface. The last process includes adsorption of gaseous species, which eventually react with the surface atoms, desorption of volatile species generated in the solid lattice and sputtering due to energetic particles, mainly ions impinging onto the surface after being accelerated by the sheath at the walls. A detailed simulation of the reactor performances requires the knowledge of several molecular mechanisms. Some of them are only poorly known such as the ones crucially depending on the surface structure and composition (physical and chemical adsorption, sputtering yields). Moreover the active processes are each characterized by its own times and magnitude, thus implying a considerable degree of complexity. Therefore in order to keep the problem manageable some approximations are badly needed. As far as it concerns the plasma, we point out that the characteristic times ruling the discharge development are very short (for instance, when radiofrequency is employed as discharge supply unit using 13.56 MHz commercial frequency, the RF cycle period is 74 ns, the confinement time for electrons drifting to the walls is about a few µs) compared to the ones governing the radical species transport and the gas-phase reactions:
therefore the plasma produced in the reactor can be considered in a quasi-stationary state determined by the external working parameters (pressure $P$, flowrate $Q$ and discharge electric power $W$) and slowly adapting to the changes in the neutral species concentration.

Fig. 1. Chemical kinetics in a CH$_4$-Ar plasma, main chemical species and processes.

Therefore the plasma evolution decouples almost completely from gas kinetics. The chemical kinetics of plasma driven processes to be considered in the model can be then fully characterized by prescribing the correct plasma state as an external condition, setting as parameters the electron density $n_e(r,z,t)$ and their energy distribution function EEDF $f_{E}(r,z,t)$. Despite several processes are involved in the electron energy losses, due to the rich molecular structure of the gas, the measured EEDFs appear in most of the cases approximately Maxwellian and therefore can be parameterized simply by an electron temperature $T_e(r,z,t)$ making easier the comparison and the analysis (Raizer, 1991). Outside of this scheme remains the connection between such microscopic parameters and the external operative ones, which should be assured by the analysis of the experimental data or by a dedicated plasma discharge modeling. However, in general, phenomenological relations hold. For instance, at fixed pressure, the electron density $n_e$ comes out to be nearly proportional to the electric power feeding the discharge, while the electron temperature $T_e$ is almost independent of it (Rhallabi, 1991).

The problem of determining the evolution of the concentration of the different chemical species (neutral and charged) can be managed by writing the balance equation for each density $n_k(r,z,t)$ of the $k$-th species:

$$\frac{dn_k}{dt} = \Pi(n_k) - \Delta(n_k)$$  (1)
where at the left hand side there is the total time derivative. The first term \( \Pi(k) \) consists of the sum of all production processes of the \( k \)-th species, due to both chemical reactions, in the gas phase or at the reactor surface, and to the external gas fed, and it can be written as

\[
\Pi(n_k) = \sum_{i<j=1}^{N} K(i + j \rightarrow k) n_i n_j + \sum_{l=1}^{N} K(l \rightarrow l(w) \rightarrow k) n_l + Q(k(in) \rightarrow k)
\]  

(2)

where \( K \) are the reaction rates for the gas phase reactions and the effective rate for the surface ones (consisting of the chain process: adsorption of species \( l \), reaction at the surface and desorption of species \( k \)) and \( Q \) is the flow rate. In the same way the contributions to the loss term of the \( k \)-th species are the destruction of \( k \) in a gas phase reaction, the diffusion followed by adsorption at the reactor surface and the pumping outside.

\[
\Delta(n_k) = \sum_{i,j=1}^{N} K(k + i \rightarrow j) n_k n_i + D(k \rightarrow k(w)) V^2 n_k + Q(k \rightarrow k(out)) \frac{n_k}{n_{tot}}
\]

(3)

where \( D \) is the diffusion coefficient of the \( k \)-th species. In parallel a simulation of the hydrodynamical flow should also be performed, so that the right velocity field can be inserted in the total derivative in order to close the system of differential equations. For the sake of simplicity, in a preliminary stage where the focus is mainly on the chemical kinetics effects, some other approximation is worthy.

Since in normal operative conditions (for instance in a low pressure gas flow, \( P=0.1 \) mbar, \( Q=50 \) sccm (Rhallabi, 1991)) the Reynolds number is small, a simple laminar flow in a cylindrical tube is an adequate representation of the reference reactor hydrodynamics. Moreover it is in general appropriate to distinguish between cases where the flow velocity exceeds the diffusion one from the opposite. From a chemical engineering point of view, indeed it means that the model can be formulated as a plug-flow or a well-mixed reactor (Benson, 1982; Smith, 1987). The gas-phase composition in the reactor is then determined only by the chemical reactions among the reactive species and the transport processes to the walls. In low pressure cold plasmas the former is more common. As a reference, the flow velocity \( V \) in a 10 cm diameter tube, at \( P=0.1 \) mbar and \( Q=50 \) sccm, is about 1 m/s and exceeds the diffusion one (\( V_{diff} \sim D/2R \) where \( R \) is the vacuum chamber radius). Indeed the so-called Peclet number \( Pe \) is about 5. So, it is implied that a plug-flow approximation, that is neglecting diffusion in the flow direction is appropriate. As a result the geometry is slab and the total derivative simply reduces to a single derivative along the streamline \( z \). The equations can be further simplified treating the diffusion process according to a scheme discussed in literature (Chantry, 1987). It implies, in short words, in approximating the transverse (in a cylinder, radial) profile of the concentration as the first normal mode dictated by the reactor chamber geometry (in our cylindrical geometry, this leads to the use of the Bessel function \( J_0(kr) \)). Within this approximation diffusion should be considered only for species that can be absorbed at the surface (for which the so called sticking coefficient \( S \) is not zero) and its contribution to the loss term becomes

\[
D(k \rightarrow k(w)) V^2 n_k(r,z) \approx \frac{D}{\Lambda^2} n_k(z)
\]

(4)
where the coefficient $\Lambda$ depends only on geometrical factors and on the sticking coefficient $S$ of each chemical species (Chantry, 1987). This formulation leads to the substitution of the Laplacian operator with an effective diffusion length and makes the system of balance equations only dependent from a single independent variable, here the distance along the streamline, or time in a well mixed formulation. So linearized this differential equations system can be integrated by means of standard numerical techniques, for instance using an adaptive Kutta-Runge routine, or other finite elements methods (Press, 1985). Additional computing time can be saved, especially in the early steps, by using as variables the logarithm of density and of time, thus effectively smoothing the system. As a result a complete mapping of the gas-phase composition and of the flows towards the surfaces could be obtained. The bulk of the modelization then stays in the collection of the relevant reaction rates at the low pressure conditions of the experiments. The most critical are ions and electrons interactions, since coherence with the underlying plasma state could not be taken for granted. Electron detachment should be added for completeness, even if it comes out that it plays a minor role in negative ion kinetics. Diffusion coefficient for ions can be extracted from mobility studies and as far as concerns the sticking coefficients $S$, the value $S=1$ is appropriate for charged particles. The introduction of a dedicated charge balance equation avoids the unphysical violation of the quasi neutrality of the bulk plasma affecting many existing and published simulations (Kline, 1989). This is badly needed whether one would take properly into account the ion recombination on the surface. It turns out that this is an important source of radicals since new data indicate that the electron recombination of molecular ions can be a strongly dissociative process (Semaniak, 1998; Riccardi, 2000). Even in the case of ion diffusion to surfaces, ions recombine with electrons on the wall, so that neutrals are back injected in the plasma.

### 2.2 Low pressure radiofrequency plasmas

Simulation of the chemical kinetics of a CH$_4$/Ar radiofrequency (RF) discharge at low pressure, is a typical case study of cold plasmas modelling. As a reference we consider, having in mind the actual experiments performed in literature, a cylindrical vacuum chamber. The gas flows along the cylinder axis and enters the plasma region through a grid electrode. There an uniform plasma (for the sake of simplicity, however it is straightforward to include in the simulation any longitudinal profile) is present. After reaching the second electrode, the neutral gas exits the plasma region. Downstream only neutral reactions could happen. The discharge balance is supposed to be assured by the compensation of the bulk ionization rate and the radial (ambipolar) diffusion of charged particles towards the walls. For the sake of simplicity it was assumed that the steady plasma condition can be described by an uniform electron density and temperature in the discharge region. The characteristic plasma chemistry processes, which are mainly driven by high energy electrons, include ionization, dissociation with production of highly reactive free radicals and transition to excited states. Besides the rich emission spectra of the discharge, these processes produce highly reactive metastable (i.e. long lived) species. In particular argon could trigger very interesting chemical kinetics effects due to its metastables (Tosi, 1995). Such processes can be taken into account by prescribing the correct plasma state as an external condition, by setting the electron density $n_e$ and temperature $T_e$ as parameters. The model discharge parameters could be related to external operating parameters in order to make comparison with existing experiments. For instance, an electron temperature of 4 eV has been estimated from the solution of the Boltzmann equation in pure methane for radiofrequency plasmas at a power level of 50 W, a value that agrees with
experimental data (Rhallabi, 1991). A change in this parameter will affect mainly the different weight of electron impact reaction channels, at first the balance of ionization and neutral dissociation. As for the estimate of the electron density, one could solve the global energy balance equation (Rhallabi, 1991). A change in this parameter will affect mainly the dissociation degree reached by the end of the plasma region. In general, during experiments it is preferred to have moderately high flow velocity and short residence times. This assures that a uniform and steady flow of precursors is delivered to the downstream target, which is mandatory whether steady deposition is needed and uniform growth of the thin film is to be assured. As discussed above the model will be formulated as a plug-flow reactor model (Benson, 1982).

2.3 Spark discharges at atmospheric pressure

The second cold plasma system whose chemical kinetics we would like to discuss is the so called spark discharge (Raizer, 1991). This kind of intermittent discharge is produced by means of a d.c. high voltage supply when it is applied between two facing metal electrodes and it is controlled with a suitable external circuitry. Sparks are rapidly quenched inhibiting transition to arc, while the produced plasma state lasts enough to efficiently process a gas flow. Below we will discuss application to hydrogen reforming using an hydrocarbon flow.

As a reference we consider a setup where the two electrodes are coaxial cylinders, the external hollow, and in the space between them the gas flows and the discharge takes place. Due to the limitation in the output current provided by the generator and the external circuit impedance, which inhibits the development of a burning d.c. arc (Raizer, 1991) the discharge assumes an intermittent character, consisting of individual events of electrical current flow of limited amplitude and time, the sparks. The system shows intense current bursts with a limited duration, separated by dead times, corresponding to a sequence of spark discharges. Although not exactly constant, both the shape, the amplitude, the duration and the repetition rate of bursts are comparable and fairly cyclic. The spatio-temporal structure of such discharge events is displayed in fig. 2, where a frame recorded by a commercial CCD camera (Nikon Coolpix-4500, 30 fps, exposure time 2 ms) is compared with the time series of the discharge current, in a spark device developed at the laboratory of the authors (Barni, 2009). While the pattern of the single discharge is somewhat fuzzy, it appears that most of the flow cross-section is affected by the discharge and emits light. This is obtained with the insertion of a high external circuitry resistance. This opens the way for a simulation of the gas phase evolution using monodimensional approximations, extending the low pressure modelling to the new situation. From the geometrical point of view, the model formulation used treats the spark channel as a rectangular prism with the axis parallel to the electric field and a square cross-section, aligned with the gas streamlines. The actual value of the spark size $l$ is treated as a free parameter of the simulation. Here the value was fixed to the experimentally estimated spark diameter, $l = 500 \ \mu$m. The contribution of the electrons to the discharge chemical kinetics depends on their local density and energy distribution. Both can be linked to the local amplitude of the electric field $E_\parallel$. Although it is possible to predict the shape of the electric field in a given electrode setup and this could depend also on the position along the spark path, the differences are not large, and we chose to neglect them, assuming uniformity along the spark path. This implies that simulations assume a constant value for both the electron density and their mean energy. In the simulations, both parameters were varied in an extended range, which
easily includes realistic values of the local electric field. In particular it includes density scaled electric field strength $E_s/N$ in the range $0-200$ Td ($1$ Td = $10^{-21}$ V m$^2$). In order to estimate the average electron density in the spark channel, we have neglected the contribution of ions to the measured discharge current. Under such approximation the current is determined by the size of the discharge section and the electron mobility as a function of the electric field, which was taken from literature for pure methane (Davies, 1989). This should be approximately right also for argon/methane mixtures, since mobility at the same electric field increases by a merely $10\%$ even in pure argon. The other parameter which affects the chemical kinetics is the mean electron energy distribution function (EEDF) in the spark channel. We have assumed a Maxwellian EEDF, described by a single parameter, the electron temperature $T_e$. This can be easily connected with the mean electron energy, which is determined by the local electric field through the Boltzmann equation (Raizer, 1991).

Fig. 2. Spark discharge in a hollow cathode setup, with the time evolution of the current.

3. Hydrocarbon plasma chemical kinetics

Methane and other light hydrocarbon plasmas are of great interest in industrial applications, in particular in the chemical vapor deposition processes (CVD) and specifically in plasma enhanced deposition (PECVD). Amorphous carbon and diamond-like thin films, suitable for mechanical and electronic applications can be prepared using low pressure discharges of hydrocarbon gases (Angus, 1988). The research in this field is mainly devoted to the understanding of the nature of the film growing mechanism but in spite of intense experimental and theoretical work it is not yet fully understood which species are responsible for the deposition process. Different growth species have been proposed, such as $\text{CH}_3$, $\text{C}_2\text{H}_2$, $\text{C}$, $\text{C}_2$, and $\text{CH}$, depending on the chemical kinetics pattern in the discharges. As an example we discuss the topic of the doping of $\text{CH}_4$ with Argon. Doping with $\text{Ar}$ or $\text{Ne}$ shows marked changes in the film properties (Gruen, 1995). This means that rare gases can significantly affect the plasma composition, opening new possibilities through their
additional ion or metastable excited atom chemical reactions. This makes largely interesting the study of the chemical kinetics in such plasmas. A significant advance was made possible after a rather complete survey of the charge exchange cross-section and its branching ratios between argon ions and methane have also been performed. As a result, a quite complete mapping of the relevant reaction rates in an Ar–CH₄ plasma now exists and it is possible to investigate the effect of the chemical kinetics in such a system and eventually to identify the gaseous precursor of the chemical species incorporated in the deposited film.

3.1 Radiofrequency plasmas in argon/methane mixtures

We have then modeled the gas-phase chemistry of a typical radio frequency CH₄/Ar plasma used for the deposition of diamond and diamond-like carbon films, with the aim of understanding the effects of the chemical kinetics of argon ions and metastable (Riccardi, 2000). Moreover, since the role of the walls and in particular of the ion transport processes is generally neglected, we have also tried to quantify its contribution to the plasma composition and to the formation of the radical species of interest. We find that the most abundant carbon containing radical is CH₃ in pure methane discharges, but it is the carbon dimer C₂ in discharges of methane highly diluted by argon. Thus we propose that the gaseous precursor of the film is CH₃ in methane plasmas, and C₂ in CH₄/Ar plasmas. This proposal resolves outstanding discrepancies between experimental observations, that can now be rationalized by considering two different growth species (Shih, 1993). The analysis is performed through the implementation of the theoretical (numerical) model for the chemical kinetics simulation of the Ar/CH₄ plasmas, discussed above. The model is able to predict the neutral and charged species densities along the vacuum chamber as a function of several parameters, like operating pressure, flowrate, feeding mixture composition, RF power. We have solved the balance equations for the density of 16 neutral species and 15 ionic species by considering 194 chemical reactions and 15 electron-ion surface recombination processes. A cylindrical vacuum chamber (22 cm-diameter) was modeled. The gas flows along the cylinder axis (z) and enters the plasma region through a grounded grid, which acts as reference electrode for the discharge. After reaching the driving electrode (located downstream and 4.5 cm apart from the grid), the neutral gas exits the plasma region, pulled by the pumping system. An uniform flowrate is then supposed everywhere. As already discussed plasma chemical kinetics is mainly determined after prescribing the correct plasma state as an external condition, by setting the electron density nₑ and temperature Tₑ as parameters. The discharge parameters considered here lie in the range 10⁸ –10¹⁰ cm⁻³ for the electron density and 3–6 eV for the electron temperature. Here we consider an electron temperature of 4 eV as a reference. Such a temperature was used also in the simulation of Ar/CH₄ mixtures unchanged. Such a choice allows to identify pure chemical effects and to distinguish them from those simply arising from the different dissociation degree. For the sake of a realistic physical picture, we cannot neglect however that it is expected that Tₑ should increase with the Ar fraction due to the higher ionization potential of argon. The conditions imagined in our setup are consistent with moderately high flow velocity (Vflow ∼ 30 cm/s for a flow rate of 120 sccm) and short residence times, of about 0.2 s. Then the plug-flow reactor model is a realistic choice for the simulations. In fact, in the low pressure range here considered (actually P = 0.2 mbar was used), the flow velocity exceeds the diffusion one, making negligible the mixing along the flow direction, as assumed in the model. The evolution of the concentration of the different N species in the gas phase is then determined by integrating each balance equation for the density nₓ of the
k-th species, along the cylindrical axis z. Densities of the most abundant neutral species in a pure CH$_4$ plasma are shown in figure. As could be expected the result is the finding that starting from pure methane the most abundant species at the end of the plasma region, are CH$_4$, H, CH$_3$, H$_2$, C$_2$H$_2$, and C$_2$H$_4$. Methyl radical is the most important reactive species that gets involved in the film deposition and growth. Atomic hydrogen will intervene mainly as an etching agent, controlling the H content in the film. The chemical kinetics pattern appears completely different when highly diluted mixtures of methane in argon are considered. Densities of the most abundant neutral species in CH$_4$ and 1% CH$_4$/Ar plasmas are shown in figure.

![Fig. 3. Evolution of the neutral gas-phase in a pure methane plasma](image)

![Fig. 4. Evolution of the neutral gas-phase in a 1% methane in argon plasma](image)
The most striking result is the finding that while starting from pure methane the most abundant species at the end of the plasma region, are CH$_4$, H, CH$_3$, H$_2$, C$_2$H$_2$, and C$_2$H$_4$, in the case of an initial composition given by 1% CH$_4$ diluted in Ar, the most abundant species in the plasma are Ar, H, C$_2$, and H$_2$. Reactions responsible for such behavior are mainly those of metastable argon. In fact Ar$^*$ increases significantly the dissociation of methane, producing CH$_3$ radicals. The chemistry of these species eventually produces C$_2$H$_2$ and C$_2$H$_4$, thus forming the strong C-C bond. Successive dissociative processes involving C$_2$H$_x$ species finally result in the production of C$_2$. This kinetic chain is inhibited by CH$_4$ and therefore proceeds only if most of methane has been dissociated. This finding is coherent with recent experimental observations indicating that high fractions of argon in H$_2$/Ar/CH$_4$ plasmas result in an increase in the C$_2$ concentration (Riccardi, 2000). Above results have been obtained by considering ion recombination and subsequent neutral species desorption from the surface.

Fig. 5. Evolution of the neutral gas-phase in different methane/argon plasmas.
The transition between a CH$_3$ to a C$_2$ dominated gas-phase happens at increasing dilution in the initial gas mixture, as it can be seen by figures above. The kinetic chain inhibition by methane could be appreciated by enlarging the horizontal axis, using a log scale. In this way the fast evolution in the initial steps could be appreciated. The formation of C$_2$H$_x$ radicals proceeds indeed only after most of methane has been dissociated. The development of the discharge gas-phase in the early times can be appreciated in figure.

![Graph](image1)

Fig. 6. Expanded evolution of the neutral gas-phase in a 1% methane in argon plasma

As for the charged species in the plasma gas-phase, they show interesting trends too. Our simulations indicate that, in pure methane, the most abundant ion species are CH$_3^+$, CH$_4^+$, C$_2$H$_4^+$ and C$_2$H$_5^+$.

![Graph](image2)

Fig. 7. Charged species in plasmas of methane and argon diluted methane.
The CH$_5^+$ ion, whose density initially appears to be comparable to that of these other ions, decreases along the flow, being quickly removed by ethylene and atomic hydrogen. This picture closely resembles the findings obtained by direct mass spectrometric analysis (Matsukura, 1996). Another important aspect concerns the ion contribution to the chemical kinetics pattern. Common wisdom favours a minor effect of ion chemistry due to very small concentrations of charged species respect to the neutral ones. Results discussed so far have been obtained by considering a null ion sticking coefficient, so that the ion recombination is taken into account and the proper neutral species are desorbed from the surface for each ion impinging on the walls. For comparison, next figures show the corresponding results obtained by assuming complete ion absorption. It is clear that ion recombination processes on the surface contribute significantly to the density number of a few species, in particular in pure methane about 20% of the CH$_3$ comes from the walls.

Fig. 8. Evolution of the neutral gas-phase in different methane/argon plasmas when complete ion sticking is considered.
Even more striking is the effect in the Ar/CH\textsubscript{4} plasma where the C\textsubscript{2} density is reduced by about one order of magnitude in the case of unitary sticking coefficient and the majority of carbon atoms, initially fed through CH\textsubscript{4} molecules, are adsorbed as ionic species on the walls. This is clearly at variance with the common belief that ion chemistry can be neglected as ion densities are typically lower than those of neutrals by many orders of magnitude. On the contrary, though ions are much less abundant than neutrals, the cumulative effect of the ambipolar diffusion transport cannot be neglected in those cases where the interaction with the walls is expected to play a role. At each plasma condition there is a dilution level at which a sharp transition in the final gas-phase composition happens. For our conditions it could be appreciated from the data at different Ar concentrations, reported in figure. In the end we show also the effects of physical parameters of the discharge, that is the electron density and temperature on the evolution of the gas phase. The first has only a rescaling effect, increasing the velocity of the dissociation, without affecting the transition concentration. The latter affects also the transition since the relative levels of CH\textsubscript{3} and CH\textsubscript{4} depend on the electron temperature, as it could be grasped from figure.

![Graph showing CH\textsubscript{4}, CH\textsubscript{3}, and C\textsubscript{2} densities vs. Ar concentration](image1)

![Graph showing CH\textsubscript{4}, CH\textsubscript{3}, and C\textsubscript{2} densities vs. Electron Temperature](image2)

Fig. 9. Evolution of the neutral gas-phase as a function of the electron density and temperature

### 3.2 Hydrogen reformer based on spark discharges

Hydrogen reforming from methane is up to now the most viable source for large scale as well as localized production of hydrogen for fuel cell systems. Conventional reforming is carried out thermally in oven with oxygen and steam or using catalytic beds but the development of more compact devices is actively pursued too. Electrical discharges at atmospheric pressure are widely used in applied research for instance in material surface processing and pollutant waste disposal. Their application for the promotion of chemical reactions as alternative to conventional process has emerged too. In particular atmospheric...
pressure plasmas have been suggested as hydrogen reforming devices, based on arc discharges, microwave plasmas and dielectric barrier discharges (Paulmier, 2005).

Here we present a discussion of hydrogen reforming using a pulsed spark discharge in an air/methane mixture (Barni, 2006). The simulations have been developed to help in the experimental research, using an already existing electrode setup, which was designed for burning a continous arc discharge. It consists of a cathode, an hollow pin of copper ending with a tungsten tip, and an anode, a block of copper with a shrinking cylindrical cavity surrounding coaxially the cathode (Barni, 2009). Details of the setup relevant for the model build-up are discussed briefly here. The anode is maintaned fixed at a distance from the cathode which is 1.2 mm at the closest location. A gas flow passes through the electrode gap, entering from three small holes at the beginning of the cathode. Technical (dry) air and high purity methane, were used to prepare the controlled air/methane mixtures employed. High purity methane and technical air (80% N₂, 20% O₂) have been used, to avoid contamination from impurities and water vapour in the environment atmosphere. A termocouple was inserted downstream in order to measure the temperature of the outgoing gas. No effort was made to fix the electrodes temperature, although this was technically feasible, partly because heating should increase methane decomposition and partly in order to maintain the system setup simple. Light emitted from the discharge is collected and analysed in a low resolution spectrometer. This allows to measure integrated emission spectra of the discharge, which give access to information about the composition of the produced gas-phase in the discharge. Initially the simulation targeted only argon/methane mixtures which were much simplier to simulate. Results of the modeling will be discussed here. The parameters were: a gas mixture of 4% CH₄ in argon, a flowrate Q = 2600 sccm, an electron density of 5.6 × 10¹⁵ cm⁻³ and an electron temperature Te = 2.6 eV (Barni, 2006). At such dilution a complete transformation of methane in hydrogen and carbon is obtained. Recombination of neutral radicals happens quickly downstream the discharge region, producing an outgoing flow composed of hydrogen with less than 10% of heavy hydrocarbons. The transition in the gas-phase composition is very fast (in the first 81 nm corresponding to 87 ns).

Fig. 10. Evolution of the neutral and charged gas-phase along a streamline passing through the spark.
For the discharge simulation described above the conversion factor $C$ was 94.61%. However the predicted efficiency of the device is only 0.14% which depends on the very small duty cycle of these discharges. It is interesting to notice that the chemical kinetics in the neutral gas-phase favours the polymerization of heavier hydrocarbons, here included all as $\text{C}_x\text{H}_y$ radicals, with a small hydrogen content. This is driven by a trade-off between the hydrocarbon radicals reactions, which favours the formation of C-C bonds (for instance the fast $\text{CH} + \text{CH} \rightarrow \text{C}_2\text{H} + \text{H}$) and the dissociation processes, which preferentially leads to hydrogen abstraction rather than C-C bond breaking. In next figure the conversion factor as a function of the plasma parameters is shown. The conversion factor $C$ reaches a maximum ($\sim 98\%$) and then decreases slightly, as electron density rises. A sharp drop in the conversion is observed for lower density. Indeed at a relatively low density the chemical kinetics is slowed down and complete transition cannot be accomplished before the flow exits outside the discharge region. A similar trend is reported by changing the electron temperature. Again the conversion factor is almost independent on the effective value of $T_e$ in a wide range (more than 90% for $T_e$ between 2 and 5 eV). However, for low temperatures, the conversion factor drops, reaching a mere 16.7% at 1.5 eV.

Fig. 11. Conversion efficiency of spark discharges depending on plasma parameters.

4. Conclusions

A chemical kinetics modeling scheme suitable for cold plasmas simulations has been presented. The model was used to study the chemical kinetics of hydrocarbon plasmas in particular the effect of argon dilution. The results obtained have been used to discuss the composition of the gas phase and the possible precursors for carbon thin film growth. The model was then used for atmospheric pressure spark discharges as a system for hydrogen reforming with plasmas. These examples show that important and significant aspects determined by the chemical kinetics effects could be investigated through simulations. Then they could prove worthy in order to study the applications of plasmas as processing reactors.
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6. References


Chemical Kinetics relates to the rates of chemical reactions and factors such as concentration and temperature, which affects the rates of chemical reactions. Such studies are important in providing essential evidence as to the mechanisms of chemical processes. The book is designed to help the reader, particularly students and researchers of physical science, understand the chemical kinetics mechanics and chemical reactions. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at physical science (mainly chemistry) technologists. Undoubtedly, this book contains "must read" materials for students, engineers, and researchers working in the chemistry and chemical kinetics area. This book provides valuable insight into the mechanisms and chemical reactions. It is written in concise, self-explanatory and informative manner by a world class scientists in the field.

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