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SYNTHÈSE DE NANOSTRUCTURES DE CARBONE EN UTILISANT UN RÉACTEUR À PLASMA D’INDUCTION À HAUTE FRÉQUENCE

SYNTHESIS OF CARBON NANOSTRUCTURES USING A HIGH FREQUENCY INDUCTION PLASMA REACTOR

Thèse de doctorat es sciences appliquées
Spécialité: génie chimique

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Canadä
À ma fille, Alina

À ma femme, Laura

À la mémoire de ma sœur, Hidemi
RÉSUMÉ

Les fullerènes et les nanotubes sont de nouvelles formes de nanostructures de carbone qui présentent d’importantes propriétés physiques et chimiques pour de futures applications dans les domaines de la nanoélectronique, de l’optique et de la médecine.

Ce travail aborde la recherche sur la synthèse de nanostructures de carbone. Les principaux objectifs sont: 1) l’exploration de la technologie des plasmas d’induction pour la synthèse de nanostructures de carbone en continu, et 2) la prédiction des mécanismes de formation de fullerènes au travers d’études théoriques.

La méthode utilisée dans le plan expérimental est basée sur la vaporisation de mélanges de réactants carbone-métal suivi par la condensation du gaz de carbone produit. Le montage expérimental est composé d’un réacteur à paroi refroidie équipé d’une torche à plasma induit par haute fréquence de 3 MHz.

Des études thermodynamiques théoriques ont été réalisées pour prédire la composition à l’équilibre de fullerènes sur une plage de température allant de 300 à 5000 K. Outre la prise en compte des plus récentes données thermodynamiques publiées pour les fullerènes, une nouvelle approche cinétique a été utilisée pour établir un formalisme réactionnel des espèces carbonées impliquées dans le mécanisme de formation de fullerènes. Spécifiquement, cette approche considère un mécanisme de croissance de fullerènes par addition séquentielle de molécules de C₂ et de C₃.

Une série d’expériences préliminaires a été complétée afin d’évaluer la possibilité de produire des fullerènes. Pour la réalisation de ces expériences, l’acétylène (C₂H₂), le carbone amorphe (CB) et le tétrachloroéthylène (C₂Cl₄) ont été utilisés comme source de carbone, tandis que le fer (Fe), le nickel (Ni) et l’yttrium (Y) ont agi comme catalyseurs. De plus, un plan factorial statistique a été aussi développé pour mieux comprendre l’effet des paramètres opérationnels sur le rendement du C₆₀. Les paramètres opérationnels utilisés ont été: la pression du réacteur (40 et 66 kPa), la puissance électrique (20 et 40 kW), le rapport carbone-catalyseur (2 et 4 %mol) et le débit de la matière première (2 et 4 g/min). Différents mélanges CB-Ni ont été utilisés dans les expériences.
Des mesures de spectroscopie d’émission ont été réalisées pendant les expériences de synthèse de fullerènes. En outre, l’emploi de diverses techniques analytiques comme la spectroscopie UV, la thermogravimétrie (TGA) et la microscopie électronique a été nécessaire pour analyser la sue produite dans le procédé plasma.

Les résultats théoriques et expérimentaux ont montré que l’utilisation de $C_2H_2$ comme matière première inhibe la formation de fullerènes. Par contre, des composés riches en carbone comme le carbone amorphe favorisent la formation de fullerènes. De plus, l’étude cinétique a montré qu’aux températures du plasma ($>2500$ K), la formation de fullerènes opère par addition séquentielle d’espèces $C_2$ et $C_3$. En fait, des concentrations de $C_{60}$ jusqu’à 3.6 et 2.1 en pourcentage massique ont été produites en utilisant différents mélanges CB-Ni.

L’étude sur la vaporisation des particules a montré que les bas rendements de $C_{60}$ sont liés au faible processus de vaporisation. La grandeur moyenne des particules des mélanges CB-Ni utilisés est de $100 \pm 57 \mu m$. Les plasmas d’argon et d’hélium peuvent vaporiser des particules pouvant atteindre $100 \mu m$ à une puissance de 40 kW.

L’étude statistique a montré que les conditions optimales d’opération sont une puissance de 40 kW, une pression dans le réacteur de 66 kPa, un débit de matière première de 2 g/min et un rapport CB-Ni de 2 % massique.

Des analyses au microscope électronique à transmission de la structure de la sue produite ont confirmé la synthèse de nanofibers, de nanaonions et un nanotube. Le nanotube de carbone identifié est composé de trois couches successives concentriques (MWCNTs).

En considérant les résultats présentés dans cette étude, des travaux futurs sont proposés afin de mieux comprendre les mécanismes de formation des nanotubes. Une modification des zones de réaction et de trempe de l’appareil devrait être réalisée afin de favoriser les réactions de croissance des espèces de carbone à haute température. Enfin, une étude systématique sur les interactions entre les espèces de carbone gazeuses et la surface d’autres catalyseurs devrait aussi être accomplie.
ABSTRACT

Fullerenes and nanotubes are new forms of carbon nanostructures that have exhibited important physical and chemical properties with a wide range of future applications such as in nanoelectronic, optic and medicine.

The work presented here is focused on the investigation of the synthesis of carbon nanostructures. The main objectives of this research are: 1) to explore the induction plasma technology to in-continuous synthesize carbon nanostructures, and 2) to predict fullerene formation throughout theoretical studies.

The methodology used in the experimental design is based on the vaporization of carbon-bearing reactants followed by the condensation of the carbon gas. The experimental apparatus consisted of a continuous flow type reactor equipped with a high frequency plasma torch operated at 3 MHz.

Theoretical thermodynamic studies were carried out to predict the equilibrium composition of fullerenes at several operating conditions. These studies involved the more recent thermodynamic data reported on fullerenes. Additionally, a new kinetic approach was used to evaluate the chemical kinetics behavior of the carbon species involved in the formation mechanism of fullerenes. This approach considers fullerene growth by a sequential addition of $C_2$ and $C_3$ molecules.

A series of preliminary experimental tests were conducted to evaluate the process ability to produce fullerenes. In these tests acetylene ($C_2H_2$), tetrachloroethylene ($C_2Cl_4$) and carbon black (CB) were used as carbon source and iron (Fe), nickel (Ni) and yttrium (Y) as catalyst. Additionally, a complete statistical factorial design with four factors at two levels was also developed. This design studied the effect of the system operating parameters on the $C_{60}$ fullerene yield. The operating parameters involved in the study were: 1) reactor pressure (40 and 66 kPa), 2) plate power (20 and 40 kW), 3) carbon-bearing ratio (2 and 4 %mol) and 4) raw material feed rate (2 and 4 g/min). In this study, mixtures of CB-Ni were used as raw material.

Throughout the study, emission spectroscopy analyses were performed to evaluate the overall temperature of the vaporization process and $C_2$ density. Furthermore, several techniques, such
as UV spectrophotometry, HPLC chromatography, surface area, thermogravimetric analysis and scanning and transmission electron microscopy were also used to analyze the soot produced in the plasma process.

Both theoretical and experimental results indicated that the use of C\textsubscript{2}H\textsubscript{2} as starting material inhibits fullerene growth. In contrast, highly-rich carbon compounds such as carbon black favour fullerene formation. Further, the kinetic study revealed that at plasma temperatures (T>2500 K) fullerene formation proceeds via sequential additions of C\textsubscript{2} and C\textsubscript{3} species. In fact, C\textsubscript{60} yields of about 3.6 and 2.1 %wt were synthesized when CB-Fe and CB-Ni mixtures were used as raw material, respectively.

A particle vaporization study revealed that low fullerene yields are correlated with a poor particle vaporization process. The average particle size of CB-catalyst mixtures was measured to be about 115 +/- 57 \textmu m. Only at higher plate power, argon and argon-helium plasmas were able to vaporize particle sizes of about 100-\textmu m.

The statistical study showed that the optimal operating conditions were at 40-kW of plate power, 66-kPa of reactor pressure, 2-g/min of raw material feed rate and 2-%mol of raw material-catalyst ratio.

The ultrastructure study involving scanning and transmission microscopy analyses revealed that carbon nanofibers, nano onions and one nanotube were also successfully produced. A multi-wall carbon nanotube (MWCNT) with three concentric walls was identified at different magnifications.

Overall, the findings of this study are relevant in carbon nanoparticle technology and future research is proposed to fully understand the formation mechanisms. Based in the results of this work, additional work using a modification of the plasma reactor should be performed in order to favour carbon species annealing at high temperatures. Different gas and liquid carbon-containing starting materials should be also considered to improve the vaporization process. A systematic study of the gas carbon species-catalyst interaction during the fullerene growth should be undertaken.
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CHAPTER 1 INTRODUCTION

Carbon is a very important element in almost any scientific field. For instance, carbon plays a dominant role in the chemistry of life and is found in many different compounds including food, drugs, vitamins, natural and synthetic fibers and hydrocarbons. In fact, an important branch of chemistry, organic chemistry, is devoted to the study of carbon compounds and their reactions. New carbon structures, called fullerenes and nanotubes, exhibit several important properties that have a wide range of future technological applications. The many exciting applications have increased research interest in their production and characterization.

This chapter briefly describes the different forms of carbon-only compounds. We begin with amorphous carbon and finish with fullerenes and nanotubes, which are the main subject of this work. A short description of the plasma state and its generation methods is also presented in order to frame the objective and the methodology used during the theoretical and experimental part of this work.

1.1 The Element Carbon

The carbon atom has four electrons in its valence shell and presents the electronic configuration \((1s^2)(2s^22p_x2p_y)\) in its ground state. In this way, it can form three different hybrid bonds \((sp^3, sp^2\text{ and } sp^1)\) as result of promotion and hybridization.

In the first type of hybridization, there are four equivalent \(2sp^3\) hybrid orbitals, which can form four tetrahedrally oriented \(\sigma\) bonds \((Csp^3 - Csp^3)\) by overlap with orbitals of neighboring atoms. A typical example of this configuration can be found in the molecule of methane \((CH_4)\). In the second type of hybridization, the carbon atom forms three-\(sp^2\) hybrid orbitals, which are equivalent, coplanar and oriented 120° to each other, leaving one unhybridized 2p orbital. These \(sp^2\) orbitals form \(\sigma\) bonds by overlap with orbitals of others atoms, while the
remaining p orbital can form a π bond by overlap with the p orbital of another carbon atom as in the ethene molecule. The bonds formed in this way are represented as Csp² = Csp².

A special arrangement of the sp² σ bonds can be found in the aromatic carbon-carbon bond (Car–Car), exemplified by the hexagonal ring of the benzene molecule (C₆H₆). Here, the remaining p orbitals of each carbon atom overlap each other to form fully occupied π bonds. In this condition, there exists a large delocalization energy, which contributes to the molecule stability. Finally, in the third hybridization form, the carbon atom forms two linear 2sp¹ orbitals and two unhybridized 2p orbitals. Two linear σ bonds are formed when sp hybrid orbitals are overlapped with the orbitals of the neighboring atoms.

The unhybridized p orbitals of the two different carbon atoms can overlap one each other to form two π bonds as in the ethyne (acetylene) molecule C₂H₂. Csp - Csp, represents the bonds formed in this way. Some properties of the carbon bonds are shown in the Table 1.1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Order</th>
<th>Bond Length (Å)</th>
<th>Mean Bond Enthalpy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Csp³ - Csp³</td>
<td>1</td>
<td>1.53</td>
<td>348</td>
</tr>
<tr>
<td>Car - Car</td>
<td>1.5</td>
<td>1.38</td>
<td>518</td>
</tr>
<tr>
<td>Csp² - Csp²</td>
<td>2</td>
<td>1.32</td>
<td>612</td>
</tr>
<tr>
<td>Csp - Csp</td>
<td>3</td>
<td>1.18</td>
<td>838</td>
</tr>
</tbody>
</table>

1.1.1 Carbon Black

Carbon black is the name given to a narrow gamma of products. These products are composed of elemental amorphous carbon in the form of colloidal sized spherical particles coalesced into particle aggregates and agglomerates.
Carbon black is mainly obtained by the partial combustion and thermal decomposition of hydrocarbons. Thermal-oxidative processes appear by far as the most important for the production of carbon black, because they produce more than 98% of the carbon black consumed worldwide. Specifically, the furnace black process is considered to be the most modern, flexible and economical process for the manufacture of carbon black.

The different carbon black varieties produced are distinguished from each other by their particular physical characteristics. These may include specific surface, particle size, aggregate and agglomerate structure, blackness, tinting strength, etc.

1.1.2 Graphite

Graphite is one of the most common crystalline forms of carbon. The graphite crystal structures are the well-known hexagonal and rhombohedral arrays of carbon atoms. These arrays are grouped in planar layers presenting three-coordinate $sp^2$ $\sigma$ bonding and delocalized $\pi$ bonding. These individual layers, sometimes referred as graphene sheets, are weakly bonded to each other. They are composed of strongly bonded carbon atoms at the network vertices of regular hexagons in a honeycomb pattern. Both hexagonal and rhombohedral polytypes of graphite are formed depending on how the graphene sheets are staggered. The hexagonal or 2H polytype has staggered layers in an ABAB... sequence, while the rhombohedral or 3R polytype has the stacked layers in an ABCABC... sequence.

The properties and morphology of the graphite reflect its highly anisotropic structure. Some of these properties are summarized in the Table 1.2.

Due to the strong bonding between the carbon atoms within the layers and the weak bonding between the carbon atoms of different layers, the growth of graphite takes place predominantly along the layers edges (perpendicular to the c-axis) and only very slowly normal to the layers (parallel to the c-axis).
1.1.3 Diamond

Diamond is considered to be one of the most beautiful gemstone. It has exceptional brilliance and lustre due to its high dispersion and high refractive index. In fact, diamond has the highest reflectance and index of refraction of any transparent substances. From an industrial and scientific point of view, diamond is interesting for its range of exceptional properties. For instance, diamond is the hardest known material; it is also the least compressible, and the stiffest material. It is also the best thermal conductor with an extremely low thermal expansion, chemically inert to most acids and alkalis, transparent from the deep UV through the visible to the far infrared, and is one of the few materials known with a negative electron affinity (or work function). One consequence of the negative electron affinity is that diamonds repel water, but readily accept hydrocarbons such as wax or grease. Although some diamonds are semiconductors, they do not conduct electricity well.

Diamond is made up of repeating units in which carbon atoms are joined to four other carbon atoms by sp³ σ bonds. Each carbon atom is equidistant from its neighboring carbon atoms producing a rigid tetrahedral network. The stability and rigidity of the carbon network give the diamond its unique properties shown in Table 1.2.

The crystal structure of a diamond is a face-centered cubic or FCC lattice, where each carbon atom links four other carbon atoms in regular tetrahedrons. Based on the cubic form and its highly symmetrical atom arrangement, diamond crystals can develop into several different shapes, known as crystal habits. The most common crystal habit is the eight-sided octahedron or diamond shape. However, diamond crystals can be also found in cubes or dodecahedral shapes.

1.1.4 Fullerenes and Nanotubes

Other interesting crystalline carbon structures fall in the fullerene and nanotube family. Fullerenes and nanotubes are described in detail in Chapter 2 and therefore in this chapter only a brief outline of their structures is presented for comparison with other carbon forms.
Fullerenes are usually referred as the third carbon allotrope. They were discovered by Kroto et al. (1985) in the carbon vapor produced during the laser ablation of graphite. Using a mass spectrometer, they detected that the carbon vapor produced was mainly composed of species with peaks corresponding to 720 and 840 atomic mass units. They theorized that these peaks corresponded to the C\textsubscript{60} and C\textsubscript{70} molecules, and that C\textsubscript{60} presented a truncated icosahedron structure resembling a soccer ball. Kroto et al. named this C\textsubscript{60} molecule buckminsterfullerene after Buckminster Fuller, an architect and constructor of similarly shape geodesic domes. Fullerene is the generic name used for carbon structures formed of pentagons and hexagons. A typical representation of C\textsubscript{60} fullerene structure is shown in Figure 1.1.

![Figure 1.1 Typical Structure of C\textsubscript{60} Molecule (Lauher, 2002)](image)

Fullerenes have a number of unique properties that hold promise as raw materials for a wide range of potential applications. They are perfectly spherical and contain a protected internal cavity of about 0.7 nm that can be doped with other molecules, they have a high electronegativity, they are soluble in organic compounds, they are chemically reactive; and they can be transformed into other carbon forms such as diamond.
The Table 1.2 shows a limited comparison of the physical properties of C\textsubscript{60} fullerene with the other crystalline carbon forms such as diamond and graphite. In this table, it is important to remark an abnormal high melting point for graphite. However, this value is taken as reported by the reference.

Carbon nanotubes (CNTs) are very large carbon macromolecules and can be considered derivatives of carbon fibers and fullerenes. CNTs can be seen as hexagonal lattice graphitic sheets rolled into a cylinder. Hollow carbon fibers were reported by Endo (1988) for the first time. However, the discovery of carbon nanotubes has been granted to Iijima (1991). Iijima reported their formation while studying the surface of the carbon electrodes used in an arc plasma reactor during the production of fullerenes.

<table>
<thead>
<tr>
<th>Property</th>
<th>Diamond (cubic)</th>
<th>Graphite (hexagonal)</th>
<th>C\textsubscript{60} (fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length, pm</td>
<td>154</td>
<td>142, 335</td>
<td>146, 144</td>
</tr>
<tr>
<td>Density, g/cm\textsuperscript{3}</td>
<td>3.52</td>
<td>2.26</td>
<td>1.72</td>
</tr>
<tr>
<td>Bulk modulus, GPa</td>
<td>442</td>
<td>286</td>
<td>6.8</td>
</tr>
<tr>
<td>Young’s modulus, GPa</td>
<td>1054</td>
<td>1020, 36.3</td>
<td>16</td>
</tr>
<tr>
<td>Melting point, K</td>
<td>4500</td>
<td>4450</td>
<td>1180</td>
</tr>
<tr>
<td>Thermal conductivity, W/m K</td>
<td>15000</td>
<td>2800</td>
<td>0.4</td>
</tr>
</tbody>
</table>

There exist two types of nanotubes: single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). The classification depends on the number of carbon layers in the configuration. Typical MWCNTs dimensions are: inner diameter, 1-3 nm, outer diameter, 2-20 nm, and lengths of approximately 1 \( \mu \)m. The SWCNTs structure depends on the orientation of the hexagons with respect to the tubular axis. The different orientations are comprised into the zig-zag and armchair forms. The Figure 1.2 shows a structure of a single-wall carbon nanotube.
Carbon nanotubes are highly efficient electrical and thermal conductors, and have a tensile strength hundred times higher than steel. Such properties have potential applications in flat-panel displays, high-strength cable, conductive polymers and composite materials.

![Typical Structure of a Single-Wall Carbon Nanotube](image)

**Figure 1.2** Typical Structure of a Single-Wall Carbon Nanotube, (RUTGERS Gallery, 2002)

Fullerenes and nanotubes are currently produced in carbon vapor formed by laser ablation, electric arc or hydrocarbon combustion. They are collected along with the soot and other condensable compounds by cooling and filtration. Fullerenes are purified from the soot by an extraction-filtration process with organic solvents and separated by mass using chromatographic methods. Nanotubes are purified by washing, drying and combusting the remaining soot in the filter. These production and purification processes are considered uneconomical due to the low yield and production rate.

### 1.2 Thermal Plasma

A plasma gas consists in a mixture of electrons, ions and neutral species. Although there are negative and positive free charges, they compensate each other in such a way that the plasma
becomes electrically neutral. This plasma property is known as quasi-neutrality. In comparison to an ordinary gas, the free charges of the plasma enhance the relatively high electrical conductivity. The plasma conductivity may even surpass that of metals.

Plasmas can be generated by a process known as electrical breakdown, which consists in passing an electric current through a gas in order to produce a given percentage of charge carriers and make the gas electrically conducting.

Plasmas can be produced by many different ways depending on the application. For instance, plasma can be produced by electric discharge, electrodeless radio frequency (RF) discharges, by shock waves, by microwaves, by laser or high-energy beams. Specifically, plasmas produced by electric discharges are divided in two categories as shown in Figure 1.3.

![Figure 1.3 Typical Ranges of Electron Densities and Temperatures for Thermal and Non-Equilibrium Plasmas. Adapted from Boulos, 1991](image)

The first category is called an equilibrium or thermal plasma. These plasmas are characterized by their high-energy density and the equality between the temperature of the heavy species and the electrons \((T_h = T_e)\). In other words, the thermodynamic state of the plasma approaches a local thermodynamic equilibrium (LTE). In addition, thermal plasmas are also characterized
by having a relatively high electron density range of $10^{21} - 10^{28}$ m$^{-3}$ and low electron energies in the range of 1 - 2 eV. Plasmas produced in high-intensity arcs and plasma torches or in radio frequency (RF) inductively coupled discharges are typical thermal plasma examples.

The second plasma type is known as non-equilibrium or cold plasma. These plasmas are characterized by their low-energy density and the large differences between the temperature of the electrons and heavy particles ($T_e \gg T_h$). Cold plasmas are also characterized by their low electron densities (less than $10^{20}$ m$^{-3}$) and their high electron temperatures, which can reach several electronvolts. Typical cold plasma examples are those produced in low-pressure RF and in glow and in corona discharges.

The following sections will focus on the physical characteristics of the generating devices for thermal plasma for which we are mostly concerned.

Figure 1.4 DC Thermal Plasma Torch, (NASA, 2002)

Among the most commonly used plasma-generating devices in material and synthesis processes are the direct current (DC) plasma torch and the RF inductively coupled plasma torch. Examples are shown in Figure 1.4 and 1.5, respectively. These torches operate simultaneously as a source of activated species and thermal energy, which is utilized in material synthesis and processing.
Figure 1.5  Radio Frequency Inductively Coupled Plasma Torch, (CRTP, 2002)

The use of plasma torches in the industry must satisfy the following requirements (Fauchais and Vardelle, 1997):

a) Ability to use different gases such as inert gases (Ar, He) or chemically active gases (N₂, H₂, O₂, air and CH₄);

b) Sufficiently long electrode life (20 - 1000 h);

c) Ability to control the gas enthalpy or the heat transferred to the material;

d) Acceptable losses in the torch cooling. About 50% for low-power devices (P<60 kW) and less than 10% for high-power devices (P>500 kW).

1.2.1  DC Plasma Torches

DC plasma-generating devices produce a high-temperature jet, which is used for the synthesis or processing of materials. DC plasma torches comprise three main elements; the cathode, the
plasma-forming gas injection and the anode. Two different DC torch types are commonly used: torches with *hot* cathode and torches with *cold* cathode. *Hot* cathode torches have a thoriated tungsten (2 wt% ThO₂) cathode and annular copper anode. They are used at power level below 100 kW and cannot be used with oxidizing plasma-forming gases since they damage the tungsten cathode. The second torch type uses cold copper electrodes for both cathode and anode in a co-axial tubular arrangement. The co-axial electrodes are separated by small gap in which the plasma-forming gas is introduced. A strong vortex motion is used to ensure the continuous motion of the arc root. These DC torches allow the use of oxidizing plasma-forming gases. Some typical performance parameters of the DC plasma torches are given in Table 1.3.

1.2.2 RF Inductively Coupled Plasma Torches

In RF-induction plasma torches, the energy coupling to the plasma is accomplished by the electromagnetic field produced by an induction coil (Boulos 1985, 1992 1997). In these torches, the plasma-forming gas does not come in contact with any kind of electrode. In this way all possible contamination sources are eliminated. These torches also allow the use of a wide range of plasma-forming gases including corrosives atmospheres. A typical RF plasma torch is usually constructed of water-cooled quartz or ceramic plasma confinement tube. The tube is surrounded by 3 to 7-turn induction coil. The induction coil is connected to the RF power supply through the tank circuit. Figure 1.5 shows a quartz tube induction plasma torch developed at the Centre de Recherche en Technologie de Plasmas (CRTP) in the Université de Sherbrooke. The stability of the discharge in the center of the coil is ensured by the use of three gaseous streams introduced upstream of the torch through a gas distributor head. The different gaseous streams are the sheath gas, the intermediate gas and the powder gas. The sheath gas protects the plasma confinement tube by reducing the heat flux from the plasma to the ceramic tube walls. The intermediate gas is introduced into the discharge with both axial and tangential velocity components to stabilize the plasma. The powder gas is injected axially to the center of the discharge using a water-cooled probe, and carries the material to be treated.
During the technical selection of the plasma system to be used in the experimental part of this work, several advantages of the RF plasma torch were glimpsed. These advantages may be summarized as follow:

a) The induction plasma presents a relatively larger plasma volume. This favours high throughputs of reactant.

b) A better control of the processing conditions at high throughputs is achieved thanks to the low velocity of the discharge and the easy access for the axial injection of raw materials into the plasma.

c) The absence of electrodes allows the use of a wide range of plasma-forming gases including inert, reducing, oxidizing and corrosives.

d) The long residence time of the particles into the discharge makes the induction plasma an ideal system for in-flight melting and vaporization of relatively large metal and ceramic powders.

Additionally, Table 1.3 shows a performance comparison between the DC and the RF inductively coupled plasma torches.

### TABLE 1.3 | COMPARISON OF SOME PERFORMANCE CHARACTERISTICS OF TYPICAL DC AND RF INDUCTIVELY COUPLED PLASMA TORCHES

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>DC Plasma Torch</th>
<th>RF Plasma Torch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Temperature, K</td>
<td>12,000 (a)</td>
<td>10,000 (a)</td>
</tr>
<tr>
<td>Velocity, m/s</td>
<td>400 – 600 (a)</td>
<td>10 – 20 (a)</td>
</tr>
<tr>
<td>Hot Core Volume, mm³</td>
<td>800 (a)</td>
<td>6X10⁴ – 3X10⁵ (c)</td>
</tr>
<tr>
<td>Residence Time, ms</td>
<td>0.5 (a)</td>
<td>10 – 20 (a)</td>
</tr>
<tr>
<td>Overall Energy Efficiency, %</td>
<td>60 – 80 (b)</td>
<td>40 – 60 (b)</td>
</tr>
</tbody>
</table>

b) Pfender et al., 1987.
c) Boulos, 1992.
1.3 Objective of the Study

In the decade following the discovery of fullerenes (Kroto et al., 1985) and nanotubes (Iijima, 1991), there has been an increased research interest in their production.

There is a large array of potential applications for the fullerenes and nanotubes, however present use is limited due to production expense. Systematic efforts must be undertaken in order to improve their synthesis and characterization techniques. These efforts should also include evaluation of kinetic mechanisms involved in the formation of these kinds of carbon nanoparticles (CNP’s).

Because of its remarkable properties such as high temperature and activated species density, the plasma approach is emerging as one of the most promising technologies for the production of carbon nanostructures.

The objective of this work is to further explore and study the production of fullerenes using radio frequency (RF) inductively coupled plasma technology. The method is based on the evaporation of carbon and catalyst particles using a RF plasma torch to activate the carbonaceous precursor species.

The study comprises seven sections: the introduction to the study, the bibliographic review on fullerenes and nanotubes, the theoretical thermodynamic and kinetic analyses, the experimental set-up description and the characterization techniques developed to analyze the solid products, the analysis of temperature and velocity profiles in the plasma tail, the analysis of the theoretical and experimental results and the analysis of carbon nanostructures by microscopy.

Chapter 1 briefly describes the different forms of the carbon-only compounds and the different methods to generate thermal plasmas. Special attention is given to the plasma technology used during the experimental part of this study.

Chapter 2 summarizes the basic aspects of the structure-properties relationships and formation mechanisms of fullerenes and nanotubes. This chapter also includes descriptions of current production methods with their associated costs.
Chapter 3 discusses theoretical thermodynamic and kinetic studies under different operating conditions to better understand the formation mechanisms of fullerenes.

Chapter 4 details the experimental set-up and characterization techniques used during the synthesis of fullerenes and nanotubes. Characterization techniques used during the experiments were: in-situ emission spectrometric analysis for estimation of the overall temperature of the vaporization process, UV spectrophotometry to quantify the C$_{60}$ concentration, and scanning and transmission electron microscopy to evaluate the morphology and structure of carbon nanostructures.

Chapter 5 includes the analysis of temperature and velocity profiles in the plasma tail using the results of theoretical modelization. This chapter also includes a study on the vaporization of raw material agglomerates and the estimation of the residence time of carbon species in the plasma and reactor zone.

Chapter 6 includes the analysis, interpretation and discussion of both theoretical and experimental results. This chapter describes the relationships between the operating conditions and the fullerene content synthesized. This provides sound foundation for the establishment of optimal operating parameters for improving fullerenes content.

Chapter 7 includes the interpretation of TEM images in terms of the various carbon nanostructures produced during the synthesis of fullerenes.
CHAPTER 2  BIBLIOGRAPHIC REVIEW ON FULLERENES AND NANTOTUBES

Owing to this work is focused to the synthesis of carbon nanostructures, it is important to have a deep knowledge of their physical and chemical nature before beginning experimental work. The aim of this chapter is to briefly review the structure-property relationships for fullerenes and nanotubes.

The first section of this chapter describes basic aspects of the structure and properties of fullerenes and nanotubes. The second part deals with the formation mechanisms and the main production methods. Special attention is given to the nanotube's formation pathways catalyzed by solids. The last part reviews potential applications for both fullerenes and nanotubes and the associated costs.

2.1 Fullerenes

By definition (Goodson et al., 1995, Yakobson and Smalley, 1997), a fullerene is a carbon cluster with an even number greater than 20 of carbon atoms in form of convex closed-cage containing only hexagonal and pentagonal faces. In this context, the heptagons are considered as defects because they are responsible for the concave parts of the molecule. According to the Euler’s theorem, each fullerene (Cₙ) molecule consists of 12 pentagons and m hexagons, following the relation:

\[
m = \frac{(n - 20)}{2}
\]  

(2.1)

Where \( n \) is the number of carbon atoms that form the fullerene molecule.
Therefore, the C_{60} fullerene is composed by a total of 32 faces, 12 of which are pentagons and 20 are hexagons. In turn, C_{70} fullerene is composed by 12 pentagons and 25 hexagons. C_{60} and C_{70} fullerenes have been the more widely studied molecules due to the ability to produce and isolate them in macroscopic quantities. The preparative method was initially developed by Krätschmer et al. (1990). Others fullerenes such as C_{76}, C_{78}, C_{82}, C_{84}, C_{90} and C_{96} have been already identified and isolated using chromatographic techniques (Kikuchi et al., 1992, Jinno et al., 1995). Characterization of these molecules has been a difficult task because of the small pure quantities recovered.

2.1.1 C_{60} Fullerene

Perhaps one of the most studied molecules during the past decade is the C_{60} fullerene due to its amazing configuration, properties and potential applications. Examples of these applications are its perspective use in optics, diamond film production, batteries, xerography, electronics and pharmaceutical.

Figure 2.1 Molecular Structures of Fullerenes: a) C_{60} and b) C_{70}. Adapted from Lauher, 2002)
In the C_{60} molecule, each carbon atom is bonded to three others by two longer bonds with length about 145 pm (Csp³ - Csp³ bond) and one shorter bond (Csp² = Csp² bond) with length about 139 pm. The single bonds lie between one hexagon and one pentagon are known as 6:5 bonds. Double bonds link two hexagons and are known as 6:6 bonds. The structure of the C_{60} molecule is shown in Figure 2.1.

Bakowics and Thiel (1991), and Murry et al. (1993) through experimental data and quantum computations have shown that the I_h symmetry group characterizes C_{60} molecule. Some of the C_{60} fullerene features are summarized in Table 2.1.

### TABLE 2.1  TYPICAL C_{60} FULLERENE FEATURES

<table>
<thead>
<tr>
<th>Features</th>
<th>C_{60}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentagons</td>
<td>12</td>
<td>a</td>
</tr>
<tr>
<td>Hexagons</td>
<td>20</td>
<td>a</td>
</tr>
<tr>
<td>Faces</td>
<td>32</td>
<td>a</td>
</tr>
<tr>
<td>Symmetry</td>
<td>I_h</td>
<td>a</td>
</tr>
<tr>
<td>Hybridization</td>
<td>Sp²</td>
<td>a</td>
</tr>
<tr>
<td>π-Bonds</td>
<td>30</td>
<td>a</td>
</tr>
<tr>
<td>C – C Distance, (Å)</td>
<td>1.45</td>
<td>a</td>
</tr>
<tr>
<td>C = C Distance, (Å)</td>
<td>1.38</td>
<td>a</td>
</tr>
<tr>
<td>Diameter, (nm)</td>
<td>~0.7</td>
<td>a, b</td>
</tr>
<tr>
<td>Total Energy of the C – C Bond, D_{0}(C_{60}), (kJ/mol)</td>
<td>40,390.2</td>
<td>c</td>
</tr>
<tr>
<td>Mean Energy of the C – C Bond, D_{0}(C_{60})/90, (kJ/mol)</td>
<td>448.78</td>
<td>c</td>
</tr>
<tr>
<td>Decomposition Temperature, (°C)</td>
<td>650 - 700</td>
<td>a</td>
</tr>
<tr>
<td>Color of Toluene Solution</td>
<td>Purple</td>
<td>a</td>
</tr>
</tbody>
</table>

Data reported by (a) Geckeler and Samal, (1999), (b) Kroto et al., (1985) and (c) Belousov et al., (1997)

2.1.2  C_{70} Fullerene

The next highest stable member of the fullerene family is the C_{70} molecule, which is found mixed with the C_{60} in the soot produced in almost all the fullerene synthesis processes.

The C_{70} fullerene structure, which was studied using different analytic techniques (McKenzie et al., 1992, Blinc et al., 1993), has an ellipsoidal shape described by the D_{3h} symmetry group.
This symmetry consists of an elongated fifth-order axis \((C_5)\), five second-order axes \((C_2)\), and a mirror plane \((\sigma_h)\) perpendicular to the \(C_3\) axis. In contrast with \(C_{60}\), the \(C_{70}\) fullerene presents five inequivalent types of carbon atoms, for which the \(C - C\) bonds length varies from 1.37 to 1.47 Å. The longest \(C - C\) bonds are those within the five-member ring and the shortest are found connecting the vertices of two pentagons. Some typical features are summarized in Table 2.2.

### TABLE 2.2 TYPICAL \(C_{70}\) FULLERENE FEATURES

<table>
<thead>
<tr>
<th>Features</th>
<th>(C_{70})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentagons</td>
<td>12</td>
<td>a</td>
</tr>
<tr>
<td>Hexagons</td>
<td>25</td>
<td>a</td>
</tr>
<tr>
<td>Faces</td>
<td>37</td>
<td>a</td>
</tr>
<tr>
<td>Symmetry</td>
<td>(D_{5h})</td>
<td>a</td>
</tr>
<tr>
<td>(C - C) Bonds, (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atoms 1 – 1 (number of bonds = 10)</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>Atoms 1 – 2 (number of bonds = 10)</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>Atoms 2 – 3 (number of bonds = 20)</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>Atoms 3 – 3 (number of bonds = 10)</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>Atoms 3 – 4 (number of bonds = 20)</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>Atoms 4 – 4 (number of bonds = 10)</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>Atoms 4 – 5 (number of bonds = 20)</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>Atoms 5 – 5 (number of bonds = 5)</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>Equatorial Diameter, (Å)</td>
<td>6.94</td>
<td>a</td>
</tr>
<tr>
<td>Height, (Å)</td>
<td>7.8</td>
<td>a</td>
</tr>
<tr>
<td>Total Energy of the (C - C) Bond, (D_0(C_{70})), (kJ/mol)</td>
<td>45,807.75</td>
<td>a</td>
</tr>
<tr>
<td>Mean Energy of the (C - C) Bond, (D_0(C_{70})/105), (kJ/mol)</td>
<td>436.26</td>
<td>a</td>
</tr>
<tr>
<td>Color of Toluene Solution</td>
<td>Deep magenta</td>
<td>a</td>
</tr>
</tbody>
</table>

Data reported by (a) Belousov et al., (1997).

#### 2.1.3 Thermodynamic Properties of Fullerenes

It is well known that the physical and chemical nature of a substance determines its properties. Hence, the study of the thermodynamic properties of the compounds is of considerable importance. These properties are used in all the thermochemical and thermophysical computations. Extensive research on synthesis, purification and characterization has been conducted on fullerenes in the past decade. However, thermodynamic data have been
accumulated relatively slow. In addition, some contradicting thermodynamic values for fullerenes have been found in the literature. These contradictions seem to be mainly related to the synthesis and purification processes of fullerenes.

Korobov and Sidorov (1994), Diki and Kabo (2000), Lebedev (2001) and Markov et al. (2001) have performed extensive reviews on the thermodynamic properties of fullerenes. These authors have taken into account the sample purity, the synthesis and purification processes and the analytical methods used. The following data are the recommended values for the thermodynamic properties of fullerenes.

\[ \text{a) Enthalpies of Formation} \]

The standard molar properties are fundamental thermodynamic values of a chemical compound. For instance, the standard molar enthalpy can be used to estimate the stability of a fullerene molecule and act as a criterion in the reliability of a given structure. Some experimental and estimated values for standard enthalpies of fullerenes are summarized in Table 2.3.

**TABLE 2.3** STANDARD ENTHALPIES OF COMBUSTION, FORMATION AND SUBLIMATION OF FULLERENES AND TRANSITION ENERGIES IN THE CONDENSED STATE

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H_f^0 ) (kJ/mol)</th>
<th>( \Delta H_{f}^0 ) (kJ/mol)</th>
<th>( \Delta H_{s}^0 ) (kJ/mol)</th>
<th>( \Delta H_{r} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(_{60}) (a)</td>
<td>C(_{50}) (a)</td>
<td>C(_{70}) (a)</td>
<td>C(_{70}) (a)</td>
</tr>
<tr>
<td>( \Delta H_f^0 )</td>
<td>-956 ± 12</td>
<td>-101 ± 22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta H_{f}^0 )</td>
<td>2346 ± 12</td>
<td>2530 ± 13</td>
<td>2555 ± 22</td>
<td>2931 ± 6</td>
</tr>
<tr>
<td>( \Delta H_{s}^0 )</td>
<td>183.7 ± 5.1</td>
<td>200 ± 6.1</td>
<td>206 ± 4</td>
<td>225 ± 6</td>
</tr>
<tr>
<td>( \Delta H_{r} )</td>
<td>7.46 ± 1.5</td>
<td>3.22 (277.4 K)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.15 (260.7 K)</td>
<td>2.7 ± 0.4 (340 K)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Data reported by (a) Diky and Kabo (2000), (b) Brunetti et al. (1997) and (c) Cioslowski et al. (2000).
b) Heat Capacity, Enthalpy, Entropy and Gibbs Functions of Fullerenes

The heat capacity of a substance is one of the most important thermodynamic properties because it contains essential information related to the phase transition. In addition, the dependence of heat capacity on temperature allows calculating the magnitude of the thermal effects on the energetic characteristics. For example, when the heat capacity is measured at temperatures lower than 5 K, it is possible to estimate the enthalpy, entropy and Gibbs function for a wide temperature range.

Table 2.4 shows the polynomial equation coefficients (equation 2.2, 2.3 and 2.4) for the molar heat capacity, enthalpy and entropy of fullerenes. These equations were fitted using the thermodynamic data reported by Diky and Kabo (2000) for C\textsubscript{60} and C\textsubscript{70}, and Brunetti et al. (1997) for C\textsubscript{76} and C\textsubscript{84} fullerenes. In these relationships, the mass is in moles, the energy is in joules and the temperatures are in Kelvin. The correlation coefficient and standard error for C\textsubscript{60}, C\textsubscript{70}, C\textsubscript{76} and C\textsubscript{84} were estimated as 0.9925, 48.14; 0.9920, 57.81; 0.9999, 58.42 and 0.9999, 58.12, respectively.

\[ C^0_p = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \]  (2.2)

\[ H^0 = a_1 T + \frac{a_2}{2} T^2 + \frac{a_3}{3} T^3 + \frac{a_4}{4} T^4 + \frac{a_5}{5} T^5 + a_6 \]  (2.3)

\[ S^0 = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \]  (2.4)

Other thermodynamic properties are easily calculated in terms of \( C^0_p \), \( H^0 \) and \( S^0 \). For example, the internal and the standard-state Gibbs free energy can be estimated using the equations 2.5 and 2.6.
### TABLE 2.4  COEFFICIENTS OF THE POLYNOMIAL FIT FOR THE THERMODYNAMIC FUNCTIONS OF FULLERENES

<table>
<thead>
<tr>
<th></th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3 \times 10^3$</th>
<th>$a_4 \times 10^6$</th>
<th>$a_5 \times 10^9$</th>
<th>$a_6 \times 10^3$</th>
<th>$a_7$</th>
<th>ΔT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60(s)}</td>
<td>-2.7573</td>
<td>0.7739</td>
<td>5.5388</td>
<td>-9.0911</td>
<td>4.0757</td>
<td>6.0512</td>
<td>38.1542</td>
<td>0 - 1000</td>
</tr>
<tr>
<td>C_{60(g)}</td>
<td>-93.8125</td>
<td>2.4131</td>
<td>-1.3508</td>
<td>0.3146</td>
<td>-0.0257</td>
<td>2462.0400</td>
<td>416.2497</td>
<td>0 - 5000</td>
</tr>
<tr>
<td>C_{70(s)}</td>
<td>-21.2336</td>
<td>2.3006</td>
<td>-0.6248</td>
<td>-2.5581</td>
<td>1.1572</td>
<td>-19.8147</td>
<td>-119.6997</td>
<td>0 - 1000</td>
</tr>
<tr>
<td>C_{70(g)}</td>
<td>-111.0715</td>
<td>2.8404</td>
<td>-1.5945</td>
<td>0.3717</td>
<td>0.0304</td>
<td>2675.2362</td>
<td>466.8119</td>
<td>0 - 5000</td>
</tr>
<tr>
<td>C_{76(g)}</td>
<td>-441.1117</td>
<td>4.7736</td>
<td>-4.1592</td>
<td>1.6935</td>
<td>-0.2636</td>
<td>2877.9042</td>
<td>1921.0718</td>
<td>298 - 2000</td>
</tr>
<tr>
<td>C_{84(g)}</td>
<td>-421.9925</td>
<td>4.9078</td>
<td>-4.0815</td>
<td>1.5859</td>
<td>-0.2354</td>
<td>2995.0375</td>
<td>1829.8209</td>
<td>298 - 2000</td>
</tr>
</tbody>
</table>

\[
U^0 = H^0 - RT
\]  \hspace{1cm} (2.5) \hspace{1cm}

\[
G^0 = H^0 - TS^0
\]  \hspace{1cm} (2.6) \hspace{1cm}

c) *Vapor Pressures of Fullerenes*

To date, several experimental studies (Piacente et al., 1996, 1997, and Brunetti et al., 1997) have been performed on the sublimation thermodynamics of fullerenes. Here, the fullerene vapor pressure has been expressed in the form of the equation 2.7. The pressure is in kPascal and the temperature is in Kelvin. Table 2.5 shows the values and the standard error for various fullerene molecules.

\[
\log p = A - \frac{B}{T}
\]  \hspace{1cm} (2.7) \hspace{1cm}

21
TABLE 2.5 COEFFICIENTS OF THE SATURATED VAPOUR PRESSURE EQUATION OF FULLERENES

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>A</th>
<th>B</th>
<th>ΔT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60}</td>
<td>8.28 ± 0.20</td>
<td>9154 ± 150</td>
<td>730 - 900</td>
</tr>
<tr>
<td>C_{70}</td>
<td>8.38 ± 0.15</td>
<td>9917 ± 160</td>
<td>783 - 904</td>
</tr>
<tr>
<td>C_{76}</td>
<td>8.23 ± 0.20</td>
<td>10150 ± 150</td>
<td>851 - 1069</td>
</tr>
<tr>
<td>C_{84}</td>
<td>7.92 ± 0.30</td>
<td>10950 ± 300</td>
<td>920 - 1190</td>
</tr>
</tbody>
</table>

2.2 Carbon Nanotubes

Carbon nanotubes (CNTs) are considered derivatives of carbon fibers and fullerenes. Nanotubes fall into two categories. The first kind consists of graphene nanotubes known as single wall carbon nanotubes (SWCNTs). These SWCNTs have an average diameter of 1 to 2 nm and are several micrometers in length. The second kind of nanotubes is known as multi-wall carbon nanotubes (MWCNTs). MWCNTs are composed of two or more concentric cylindrical shells separated by 0.345 nm. This is slightly larger than the separation of 0.335 nm found between graphite layers. Figure 2.2 shows the schematic representation of a SWCNT and a MWCNT.

2.2.1 Carbon Nanotubes Shape and Structure

The chiral angle $\theta$ and the chiral vector $R$ given in the equations 2.8 and 2.9, respectively, can define carbon nanotube structure. For details see the 2D graphene sheet shown in Figure 2.3. Here, $n$ and $m$ are the integers and $a_1$ and $a_2$ are the unit vectors in the 2D-graphene lattice.

$$\theta = \arctan \left( \frac{-\sqrt{5}m}{2n+m} \right)$$

(2.8)
Figure 2.2 Schematic Representation of a) SWCNT and b) MWCNT. Adapted from Srivastava and Barnard, 1997

\[ R = na_1 + ma_2 \] \hspace{1cm} (2.9)

The chiral vector \( R \) connects two equivalent sites on the graphene sheet. The chiral angle is formed between the chiral vector and the zigzag direction. The graphene sheet may be thought to roll up in such a way that the nanotube is formed by the connection of its two ends through the chiral vector.

Given the chiral vector values \( n \) and \( m \), the carbon nanotube diameter can be estimated using the equation 2.10.

\[ d = 0.0783\sqrt{n^2 + nm + m^2} \text{ (Å)} \] \hspace{1cm} (2.10)
Figure 2.3  Schematic of the Index Method for SWCNTs Showing the Chiral Vector $R$ and the Chiral Angle $\theta$. Adapted from Rao et al. 2001

Figure 2.4  Schematic Representation of SWCNTs: a) Armchair Configuration, b) Zigzag Configuration and c) Chiral Configuration. Adapted from Yakobson and Smalley, 1997
The values of $n$ and $m$ determine the nanotube chirality. Three different carbon nanotube types can be found in terms of the pair $(n, m)$: 1) the zigzag tube with $n \neq 0$, $m = 0$ ($\theta = 0^\circ$), 2) the armchair tube with $n = m \neq 0$ ($\theta = 30^\circ$) and 3) the chiral tube with $n \neq m \neq 0$ ($0^\circ < \theta < 30^\circ$). These three different conformations are shown in Figure 2.4.

Chirality affects nanotube properties such as conductance, lattice structure and density. For example, if the value $n - m$ is divisible by three, the SWCNT is considered metallic, otherwise it is considered semi-conducting.

### 2.2.2 Physical Properties of Carbon Nanotubes

To date, much original research (Spires and Brown (1996), Thess et al. (1996), Gao et al. (1998), Hone et al. (1999), Hernandez and Rubio (1999)) has been devoted to carbon nanotube characterization. Nanotube physical properties are still being discovered and disputed. However, there is a general consensus about certain values as reviewed by Ebbesen (1994a, 1994b), Ajayan and Ebbesen (1997), Laurent et al. (1998), Subramoney (1998), Rao et al. (2001). Table 2.6 shows some typical SWCNT features collected by Tom Adams (2002) from the David Tomanek group at Michigan State University.

### 2.3 Formation Mechanisms of Fullerenes and Nanotubes

Despite the efforts devoted to the fullerene and nanotube study, there is no real consensus on their growth pathways. Therefore, their formation mechanisms are still unsettled. The mechanisms shown below summarize the different theories presented by researchers.

#### 2.3.1 Formation Mechanisms of Fullerenes

Early rationalizations (Kroto et al., 1985 and Zhang et al., 1986) on the fullerene formation mechanism suggested that planar graphene sheets grow by $C_2$ species addition. Graphene sheets bend to eliminate their highly energetic dangling bonds following the pentagon road rule lately proposed by Smalley (1992).
### TABLE 2.6 PHYSICAL FEATURES OF SWCNTs. (Adams, 2002)

<table>
<thead>
<tr>
<th>Equilibrium Structure</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Diameter, (nm)</td>
<td>1.20 − 1.4</td>
<td>a</td>
</tr>
<tr>
<td>Distance From Opposite Carbon Atoms (Line 1), (Å)</td>
<td>2.83</td>
<td>a</td>
</tr>
<tr>
<td>Separation of Analogous Carbon Atoms (Line 2), (Å)</td>
<td>2.456</td>
<td>a</td>
</tr>
<tr>
<td>Separation of The Parallel Carbon Bonds (Line 3), (Å)</td>
<td>2.45</td>
<td>a</td>
</tr>
<tr>
<td>Carbon Bond Length (Line 4), (Å)</td>
<td>1.42</td>
<td>a</td>
</tr>
<tr>
<td>Group Symmetry (10, 10)</td>
<td>$C_{5v}$</td>
<td>b</td>
</tr>
<tr>
<td>Lattice: Bundles of Ropes of Nanotubes</td>
<td>Triangular lattice</td>
<td>b</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>17</td>
<td>b</td>
</tr>
<tr>
<td>Lattice Parameter:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10, 10) Armchair, (Å)</td>
<td>16.78</td>
<td>c</td>
</tr>
<tr>
<td>(17, 0) Zigzag, (Å)</td>
<td>16.52</td>
<td>c</td>
</tr>
<tr>
<td>(12, 6) Chiral, (Å)</td>
<td>16.52</td>
<td>c</td>
</tr>
<tr>
<td>Density:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10, 10) Armchair, (g/cm$^3$)</td>
<td>1.33</td>
<td>c</td>
</tr>
<tr>
<td>(17, 0) Zigzag, (g/cm$^3$)</td>
<td>1.34</td>
<td>c</td>
</tr>
<tr>
<td>(12, 6) Chiral, (g/cm$^3$)</td>
<td>1.40</td>
<td>c</td>
</tr>
<tr>
<td>Interlayer Spacing:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n, n) Armchair, (Å)</td>
<td>3.38</td>
<td>c</td>
</tr>
<tr>
<td>(n, 0) Zigzag, (Å)</td>
<td>3.41</td>
<td>c</td>
</tr>
<tr>
<td>(2n, n) Chiral, (Å)</td>
<td>3.39</td>
<td>c</td>
</tr>
<tr>
<td>Electrical Transport:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductance Quantization, (kΩ)$^{-1}$</td>
<td>nx(12.9)$^{-1}$</td>
<td>c</td>
</tr>
<tr>
<td>Resistivity, (Ω-cm)</td>
<td>$10^4$</td>
<td>c</td>
</tr>
<tr>
<td>Maximum Current Density, (A/m$^2$)</td>
<td>$10^{13}$</td>
<td>c</td>
</tr>
<tr>
<td>Thermal Transport:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity, (W/m K)</td>
<td>~2000</td>
<td>d</td>
</tr>
<tr>
<td>Phonon Mean Free Path, (nm)</td>
<td>~100</td>
<td>b</td>
</tr>
<tr>
<td>Relaxation Time, (s)</td>
<td>~$10^{-11}$</td>
<td>d</td>
</tr>
<tr>
<td>Elastic Behavior</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young’s Modulus (SWCNT), (TPa)</td>
<td>~1</td>
<td>e</td>
</tr>
<tr>
<td>Young’s Modulus (MWCNT), (TPa)</td>
<td>1.28</td>
<td>e</td>
</tr>
<tr>
<td>Maximum Tensile Strength, (GPa)</td>
<td>~30</td>
<td>e</td>
</tr>
</tbody>
</table>

Data reported by (a) Spires and Brown (1996), (b) Thess et al. (1996), (c) Gao et al. (1998), (d) Hone et al. (1999), (e) Hernandez and Rubio (1999).
mass selected beams were analyzed by ion chromatography (IC). The *Arrival Time Distribution* (ATD) of the carbon isomeric species was measured in order to evaluate the mobility and fractional concentration of each isomer.

Additionally, quantum chemical methods were used to calculate the energy of different structural isomers. These energies were compared with the experimental results. This comparison helped establishing the carbon growth pattern (see Figure 2.5), which can be summarized as: *carbon atoms to linear chains (n<10) to monocyclic clusters (n>10) to bicyclic clusters (n>20) to tricyclic and more complexes clusters (n>30) and fullerenes (n>30)*, where *n* is the number of carbon atoms in the cluster. In contrast to quantum calculations, no *cup* shaped structures as C\textsubscript{20} and C\textsubscript{24} were observed in the experiments. This eliminates the idea that these species can be considered to be fullerene precursors.

![Figure 2.5](image)

**Figure 2.5** Growth Pattern for Fullerenes Proposed by von Helden et al. 1994

Aleksandrov, Shveigert et al. (1995a, 1995b, 1995c, 1996a, 1996b, and 1997) have studied carbon cluster interactions during fullerene formation. A theoretical quantum chemical study of the cluster energies was performed using the MINDO/3 method.

The system included the same types of clusters proposed in the formation model developed by von Helden et al. These clusters were linear chains, monocyclic rings, bicyclic rings, tricyclic and more complex clusters including fullerenes. They found that, for a structure with a central hexagon, the time for the first isomerization step is on the order of 10\textsuperscript{2} s and the transition
efficiency from polycyclic ring to fullerene is determined by the isomerization process kinetics. The isomerization pathway from tricyclic cluster is shown in Figure 2.6.

Figure 2.6  Isomerization of a Tricyclic Structure. Adapted from Aleksandrov, Shveigert et al., 1996b

Alekseev and Dyuzhev (1999a and 1999b) have proposed an additional fullerene formation model. This model uses tricyclic structures and assumes that fullerenes are more efficiently formed when the growing clusters capture C_2 and C_3 molecules than by isomerization as proposed by Aleksandrov, Shveigert et al.

According with Alekseev and Dyuzhev, the estimated time for triggering the isomerization process (10^2 s) is very high. In an arc discharge scheme the gas carries the tricyclic ring to the low-temperature zone of the reactor. As a consequence, fullerene formation becomes quite difficult. The capture of a C_2 molecule by the central region of a tricycle structure gives an effective push to the subsequent reactions. At the same time it assures a more uniform filling of the surface by pentagons and hexagons. The computed characteristic time for fullerene
formation was of the order of $10^3$ ms. Figure 2.7 shows the capture reaction of a $C_2$ molecule by the central part of a tricycle structure.

![Diagram showing the formation mechanism of fullerenes by initial capture reaction of $C_2$ molecule by the center of the structure](image)

**Figure 2.7** Formation Mechanism of Fullerenes by Initial Capture Reaction of $C_2$ Molecule by the Center of the Structure. Adapted from Alekseev and Dyuzhev, 1999a

Yamaguchi and Maruyama (1998a and 1998b) performed a molecular dynamic simulation using 500 isolated gas phase carbon atoms with random positions and velocities. The system was held at temperature $T_c$ of 3000 K.

The formation pathway was from simple chain and ring ($n < 20$) to tangled polycyclic structures ($20 < n < 30$) to random caged structures ($n > 30$). Imperfect $C_{60}$ and $C_{70}$ clusters were formed in the temperature 2500 to 3000 K and time ranges 1700 to 2500 ps, respectively. Theses imperfect fullerenes were held for an additional time of 200 ns at 2500 K, producing the perfect fullerene structure. Based on these simulations, the authors proposed the formation mechanism shown in Figure 2.8.

Pope et al. (1993) and Richter et al. (1999) developed a kinetic model to describe the growth of polycyclic aromatic hydrocarbons, $C_{60}$ and $C_{70}$ in flames. The mechanism is based on reaction types for ring formation as H atom abstraction, $C_2H_2$ addition and cyclization leading to ring formation, reactive coagulation of aromatic molecules and cage closing via $H_2$
elimination. A reaction temperature of 2050 K was used as representative flame value in the fullerene formation zone.

![Diagram showing fullerene formation mechanism](image)

**Figure 2.8** Fullerene Formation Mechanism Proposed by Yamaguchi and Maruyama, 1998b

Two overall pathways, called *direct* and *coagulation pathway*, for fullerene formation are depicted in Figure 2.9.

During experiments, corannulene \(C_{20}H_{10}\) was identified (Lafleur et al. 1993) using high performance liquid chromatography with UV detector and gas chromatography coupled with infrared mass spectroscopy. In contrast to the results found by von Helden et al., these results confirm the hypothesis that corannulene is a fullerene precursor. A likely explanation for this difference is that \(C_{20}H_{10}\) presents 10 hydrogen-dangling bonds, which are not present in the carbon-only *cup* shape structure. According to the authors, the thermochemical mechanism is also able to predict the formation times for fullerenes \(C_{60}\) and \(C_{70}\) in agreement with the experimentally observed times. The predicted time required for fullerene formation was about 5 ms, which was of the order of magnitude of that observed during experimentation.
Figure 2.9 Outline of the Fullerene Pathway Formation. a) Direct Pathway, b) C_{60} Coagulation Pathway and c) C_{70} Coagulation Pathway. Adapted from Pope et al., 1993

2.3.2 Formation Mechanisms of Nanotubes

At present, most of the proposed nanotube formation mechanisms have been trying to explain their growth pathways under varying operating conditions. Most prevalent are the electric arc, laser ablation and hydrocarbons flame pyrolysis. Each of these systems influences the nucleation process of the carbon species. Many reviewers support this claim, including Ajayan and Ebbesen (1997), Subramoney (1998), Laurent et al. (1998) and Rao et al. (2001). The catalyst particle also plays an important role in determining the nature of the carbon nanostructure. Therefore nanotube formation mechanisms might be divided between absence and presence of catalyst.
a) *Formation Mechanisms in Absence of Catalyst*

Endo and Kroto, (1992), have suggested that nanotubes may grow in a closed fullerene structure. This mechanism works by the insertion of smaller carbon species as C, C\(_2\) and C\(_3\) directly into the graphitic network. In the proposed mechanism shown in Figure 2.10, C\(_2\) specie is added to a six-membered ring to yield two adjacent pentagons. These pentagons diffuse into the graphite network equilibrating the structure strain and yielding a more stable configuration.

![Growing Mechanism of Nanotubes by the Insertion of C\(_2\) Specie](image)

_Figure 2.10_ Growing Mechanism of Nanotubes by the Insertion of C\(_2\) Specie. Adapted from Endo and Kroto, 1992

However, this model has not be able to explain the multi-wall nanotube growth pathways because of the difficulty in predicting inner wall growth. In this case, the open-ended growing mechanism has been considered as one of the most relevant as reviewed by Ebbesen (1994a and 1994b).

Here, the nanotube grows by the addition of smaller carbon species to reactive dangling bonds at its edge. According to Ebbesen, the growth process is kinetically favourred rather than thermodynamically at the high temperatures present in electric arc systems at which the nanotubes are formed. This kinetic process must be a result of conditions present in the arc or from a catalytic effect of a metal particle. In absence of catalyst, the current passage through the arc favours the nanotube formation with the plasma edge local field near to the nanotubes.
keeping the nanotube open during the growth. This also allows the recombination of charged species as depicted in Figure 2.11.

![Diagram showing the process of nanotube growth and recombination of charged species](image)

**Figure 2.11** Schematic Seeding and Growth of a Nanoparticle and Nanotube by Charge Recombination. Adapted from Ebbesen, 1994a

**b) Formation Mechanisms Catalyzed by Solids**

Outside of the electric field effect in the arc plasma systems, the nanotube growth takes place by catalytic action of metal particles. The overall mechanism for carbon fiber formation suggests that the growth occurs via the gas adsorption at the catalytic particle surface followed by decomposition reactions. These reactions lead to chemisorbed carbon species, carbon species dissolution and diffusion through the surface active sites, carbon species precipitation to form the carbon fiber body and the migration of the remaining carbon species around the particle surface to form the fiber skin component. The growth stops when the particles become poisoned by impurities or after a stable metal carbide formation.

Kiang and Goddard (1996) considered that the SWCNTs growth mechanism is different to those of carbon fibers and MWCNTs. They proposed a polyyne ring nucleus (PRN) growth
model for the SWCNT synthesis. The model assumes that planar carbon polyyne rings in the size range of $C_{10}$ to $C_{40}$ serve as nuclei for the nanotube formation. Nanotube diameters are related with the ring sizes. $Co_mC_n$ species act as catalyst favouring the addition of gas carbon species such as $C_2$ in the growing tube.

Figure 2.12 shows the PRN mechanism initial pathway: a) the polyyne ring acts as nanotube precursor and the cobalt carbide specie acts as catalyst; b) planar geometry deformation of the polyyne ring due to the catalyst action, producing cis and trans forms; c) non-helical tube formation with armchair configuration d) non-helical tube formation with zigzag configuration, e) helical tube formation. The first benzene ring is formed in a cis site and the growth continues on trans sites and f) another helical growth pattern.

![Figure 2.12 Polyyne Ring Nucleus Mechanism for the Growth of SWCNTs. Adapted from Klang and Goddard, 1996](image)

According to the mechanisms reviewed by Rao et al. (2001), transmission electron microscopy (TEM) analyses on the carbonaceous products obtained from the hydrocarbon and
metal particle pyrolysis show that the catalyst particle size plays an important role on the carbon product morphology. See depiction in Figure 2.13.

The figure shows that a small catalyst particle size of about 1 nm favours the SWCNTs formation while a size range from 10 to 50 nm favours the MWCNTs formation.

![Schematic Representation of the Catalyst Size Effect on the Carbon Nanostructure Produced. Adapted from Rao et al., 2001](image)

Figure 2.13  Schematic Representation of the Catalyst Size Effect on the Carbon Nanostructure Produced. Adapted from Rao et al., 2001

### 2.4 Synthesis Methods of Carbon Nanostructures

During the last sixteen years, several systematic efforts to improve the synthesis methods of fullerenes and nanotubes have been proposed. These efforts have been reviewed by Singh and Srivastava (1995), Journet and Bernier (1998), Bogdanov et al. (2000) and Churilov (2000).

One of the most useful methods to produce fullerenes and nanotubes has been graphite vaporization by laser. Graphite laser ablation in a helium atmosphere was the first method (Kroto et al., 1985) used to produce fullerene clusters in gas phase. Failure of the early attempts to yield macroscopic quantities of CNSs was mainly because the small carbon
quantity vaporized. In this condition, mass spectra's were only possible to obtain during the experiments. The new generation of laser ablation apparatus uses high temperature furnaces to improve annealing of structures in the formation of carbon nanotubes (CNTs). Figure 2.14 shows a typical laser ablation reactor. The main apparatus components are: a pulsed Nd:YAG laser operating at \(\lambda = 532\) nm with output power of about 2 J/pulse cm\(^2\), a target graphite rod as source of raw material, sometimes doped with metal particles as catalysts, an electrical oven with a quartz tube to allow a temperature about 1200 °C and a water-cooled collector to condense the carbon species and allow the growth of carbon nanostructures (CNSs).

This technique is also an efficient method to produce doped fullerenes. Chai et al. (1991), Ying et al. (1996) and Nakamura et al. (1999) have used laser ablation techniques to study the formation of metal, nitrogen and boron-nitrogen fullerenes, respectively. Although this system has shown to be an efficient technique to produce CNSs, its production rate can be considered only for research purpose.

![Figure 2.14 Laser Ablation Apparatus Used in the Production of Fullerenes and Nanotubes. Adapted from Yakobson and Smalley, 1997](image)

Graphite vaporization using a plasma arc reactor is another technique used to produce CNSs. This procedure, first used by Krätschmer et al. (1990), has shown to be able of generating large fullerene and nanotube quantities. Figure 2.15 shows a typical example of an arc
vaporization apparatus. The key components include a high current electrical source, two electrodes (at least one must be movable), and a reactor chamber with water-cooled walls to condense the carbon gas particles.

Several researchers (Huczko et al. 1995, Shi et al. 2000 and Ando et al. 2000) are using this reactor due to its ability to produce macroscopic quantities of CNSs. Operating parameters range can vary as follows: current from 40 to 150 A, pressure from 2 to 70 kPa, carbon electrodes diameter from 0.4 to 1 cm. Systems like those of Figure 2.15 may produce CNSs on scale of grams per day. This production rate remains too small for commercial use.

![Figure 2.15 Schematic of the Apparatus for the Arc Vaporization of Graphite to Produce CNSs](image)

Lange et al. (1999) performed spectrometric measurements on the plasma arc during fullerene production. They found that the maximum in C$_2$ concentration depends on the total carbon vapor pressure inside the arc for temperatures from 4000 to 5000 K. Higher fullerene concentrations were found associated with the use of higher arc currents. This result suggested the relationship between C$_2$ content and the fullerene yield of the process.

Huczko et al. (2000) studied the influence of catalyst on the formation of fullerenes and nanotubes. Typical operating conditions were: reactor pressure from 8 to 80 kPa and arc current form 64 to 79 A. Three different electrode compositions were used: pure carbon, C-Fe
and C-Co/Ni. Fullerene yield ranged from 4.5 to 10.5%. Plasma temperature and C₂ content were estimated using spectroscopic measurements. During the experiments, it was observed that the presence of catalysts into the electrode resulted in higher input compared with pure carbon electrode due to the higher electrical conductivity of electrode material and plasma. The higher plasma temperatures were observed at lower pressures independently of the anode composition. In contrast, because the lower expansion rates of carbon species, higher C₂ densities were observed at higher pressures. The results also showed that the presence of catalysts reduces C₆₀ yield at low pressures, while at higher pressures the yield is independent of the electrode composition. Fullerene yield was enhanced when Fe was used as catalysts while Co/Ni inhibited fullerene growth. Additionally, when pure carbon anode was used MWCNTs were found in the core cathode deposit and were not detected in other places in the reactor. In contrast, when carbon-catalyst anodes were vaporized SWCNTs were found in the soot recovered from the reactor walls. When iron was used as catalysts, CNTs were observed in the web-like soot surrounding the cathode deposit, while for Co/Ni catalysts CNTs were found in both the webs and the walls deposited soot.

Ando et al. (2000) developed a DC arc plasma jet method to synthesize carbon nanotubes. The experimental equipment consisted of a vacuum chamber with a Ni4%-Y1%-doped anode (6 mm in diameter). The cathode made of pure carbon (6-mm diameter) was placed 30° oblique angle from the anode. Typical operating conditions were: reactor pressure from 400 to 700 torr and arc current from 50 to 100 A. The most stable conditions were obtained under DC arc current of 60-A in He gas at 500 torr. During the experiments, three types of carbonaceous materials were obtained: 1) cotton-like carbon attached to the reactor walls, 2) a cathode deposit and 3) an aggregation-like on the tip of the cathode. The percentage of soot was 87% while the deposit percentage was 13%. SEM and HRTEM observation showed that MWCNTs were found in the cathode deposit while SWCNTs were found in the carbon aggregation. A large number of SWCNTs were also observed in the cotton-like carbon soot. The diameter ranged from 5 to 35 nm. It was established that the lower temperature gradient and the longer flight time in the high temperature region play a key role in the growth of SWCNTs.

Lange and Huczko (2001) studied the influence of nitrogen on the formation of fullerenes and carbon arc plasma. Graphite electrodes (6-mm diameter) were subjected to DC arcing in
He/N₂ gas mixtures at 13.3-kPa of pressure. Spectroscopic measurement showed that an increase in the C₂ radical content in the arc zone was observed at higher nitrogen contents. A possible explanation was that nitrogen atoms and molecules, which are heavier as compared to helium, prevent the expansion and diffusion of carbon species. The results also showed that nitrogen drastically reduce C₆₀ formations. However, nitrogen presented a positive influence in the formation of higher fullerenes (C₇₂, C₇₄ and C₈₀), which were not formed under helium conditions.

In order to improve the CNS yield and production rate, new systems based on DC plasma have been developed (Hatta and Murata 1994, Alexakis et al. 1997). The operation principle of these kinds of systems is based on the hydrocarbon thermal decomposition by means a DC plasma torch. This torch can be operated over a very wide electrical power range (5 – 50 kW).

The DC plasma torch also allows the variation of the chamber reaction atmosphere by using inert and or reactive gases as plasma gas. A DC plasma reactor used for the fullerene production via hydrocarbon dissociation is shown in Figure 2.16.

![Figure 2.16 Schematic of a DC Plasma Reactor. Adapted from Alexakis et al. 1997](image-url)
According to Alexakis (1997), theoretical studies showed that the temperature range for fullerene formation was from 2200 to 2600 °C. However, C-H and C-F bonds are also stables at temperatures between 1500 and 4000 °C. Hence, the use of hydrogen and fluorine inhibits fullerene formation due to the stability if C-H and C-F bonds in the temperature interval of fullerene formation. In contrast, C-Cl bonds are not quite stable above 1000 °C. Higher fullerene content was found when C₂Cl₄ was used as starting material. Additionally, the residence time of carbonaceous species in the temperature range of fullerene formation was found to play a key role in the synthesis of fullerenes. The residence time depended on the plasma torch power and the raw material feed rate. For instance, the estimated residence time ranged from 0.03 to 0.14 ms for a raw material feed rate of 0.29-mol/min and plasma power from 45 to 65 kW.

Another important plasma system is based on the induction technology. To date, there have already been several attempts to use RF plasma for CNS production. Peters and Jansen (1992 and 1995) evaporated various solid carbons in a high-frequency (400 Hz) helium plasma batch reactor operated using a power of 30 kW under a medium pressure (150 hPa). Fullerenes were extracted from the resulting soot with toluene yielding a 10-18 % C₆₀ content. Yoshie et al. (1992) fabricated fullerenes in hybrid plasma using various carbonaceous sources such as carbon black, benzene and acetylene. The hybrid plasma is characterized by the superposition of RF plasma and a DC arc jet operated in argon at reactor pressure from 260 to 760 torr. Typical operating conditions were 5 kW for the DC power supply and 20 kW (4 MHz) for the RF plate power input. The fullerene yield was about 7 % when carbon black was used as raw material with a feed rate of 0.5 g/min. It was observed that the plasma tail was contracted when Ar was fed as quenching gas at the end of the coil. This implied that a sufficient reaction time (> 0.1 ms) was not reached in the plasma tail. A decrease in the reactor pressure also caused a decrease in the fullerene yield. A probable reason was the poor vaporization of carbon particles at low pressure. A low reactor pressure reduces the residence time of the particles in the plasma tail. It was also suggested that hydrogen and oxygen act as inhibitor of fullerene formation because no fullerenes were found when C₂H₂ and C₆H₆ were used as starting material.
Wang et al. (2001) recently reported the synthesis of fullerenes by direct evaporation of carbon powder (20 μm) using RF thermal plasma (30 kW power). The report included spectroscopy observations on the plasma. The productivity of C₆₀ was not presented however; Si with C particles mixing had a role in enhancing the C₆₀ and higher order fullerene synthesis. According to the spectroscopic study, it was observed that fullerenes could be synthesized effectively at higher plasma gas flow conditions. According to the authors the best conditions for fullerene synthesis were: 10 kPa pressure, Ar/He/CO mixture as plasma gas at 150 l/min. An interesting observation was that 20-μm carbon particles are more suitable for fullerene synthesis than particles below 1 μm. In a further paper, Wang et al., (2002) showed that fullerene production has a relationship with the intensity of C₂ molecular and C atomic spectra. In fact, the authors thought that not only C and C₂, but C₃, C₄ and C₅ species have an influence on the fullerene production. It was also shown that the inclusion of oxygen into the reactor decreases C concentration and inhibits fullerene formation. Because reactor leaks, oxygen cannot be avoided into the reaction chamber. A large number of C species were observed to combine with O₂ to form CO and CO₂ at C/O ratio higher than 0.5.

Cota et al., (2001) used a RF plasma reactor at 50 kW to study the effect of carbonaceous raw material and catalyst feed rate on the fullerene synthesis. The highest yield (about 3.9 wt %) was obtained for the carbon-catalyst mixture. The results obtained from the thermodynamic equilibrium analysis revealed that a complete vaporization of the solid carbon is reached at temperatures about 4000 K, and that a very high concentration of the C₂ and C₃ species is observed in the temperature range from 2500 to 4500 K. No concentration was reported for C₂H₂ due to the presence of hydrogen in the reacting system. All the tests were performed in the experimental set-up showed in the Figure 2.17. The high yield of carbon nanoparticles and the lack of carbon nanotubes seemed to be associated to two main factors. The first factor was related to the size of the catalyst particle used (>5 μm) in the experiment. The second factor was related to the carbon vapor pressure-power ratio supplied into the plasma system. A carbon mass flow-power ratio of 0.6 mg/s/kW used in this study was five times lower than that of 3.0 mg/s/kW used in the conventional arc plasma processes.
Combustion flame nozzles are another useful technique for CNS production. Howard et al. (1992) detected fullerenes in the soot resulting from low-pressure oxidation of benzene and acetylene in a diffusion flame. Fullerenic formation was studied under the following ranges of flame conditions: Reactor pressure, 12-100 torr; atomic C/O ratio, 0.717-1.082; mol% Ar, He, N$_2$, 0-50; and gas velocity at 298 K, 14.6-75.4 cm/s. The results showed that fullerene formation depends on the values various operating parameters. For instance, the highest C$_{60}$ and C$_{70}$ concentrations were found about 2 cm above burner. The effect of system pressure and gas velocity showed to have a positive effect on the fullerene synthesis. Both fullerene yield and production rate were enhanced when system pressure and gas velocity were increased. Additionally, higher fullerene formation was observed when carbon vapor pressure was increased. Fullerene yield exhibited a maximum as the C/O ratio was increased. The results also showed that, consistently, helium gave higher fullerene yields than argon and nitrogen. In fact, the largest observed yield of C$_{60}$+C$_{70}$ for benzene/oxygen flames were 20% of the soot produced and 0.5% of the carbon fed. This fullerene yield was observed at 37.5
torr, a C/O ratio of 0.959, a velocity of 40 m/s and 25% helium. The authors found that fullerene formation in flames follows a growth process similar to the polycyclic aromatic hydrocarbons and soot formation. They proposed the formation mechanism shown in Figure 2.9.

More recently, Vander Wal et al. (2000) demonstrated the SWCNT synthesis via a laminar diffusion flame. In their method, metallocene was used as catalyst source to lower the energetic constraints for the SWCNT formation. Acetylene or ethylene was used as fuel. All tests were performed at atmospheric pressure and typical flow rates were 0.150 slpm of acetylene and 1.75 slpm of N₂. Metallocene was introduced with a feed rate range from 0.1 to 2 mg/min. Under these conditions, nanotubes with average diameter of 1.4 nm were synthesized. Nanotube lengths ranged from tens to hundreds of nanometers. Flame temperature and residence time were also estimated as a function of height above the burner along the axial streamline. For 8-cm of height, the maximum flame temperature was estimated to be about 1400 K, whereas the summed residence time was 50 ms. Based in the nanotube lengths and the residence time, the nanotube growth rate was estimated to be from 200-2000 nm/s.

Chemical vapor deposition (CVD) is another efficient method for direct production of macroscopic quantities of carbon nano-onions and nanotubes. According to Xie et al. (1999), very high ordered, isolated and large nanotubes can be formed on a substrate containing iron oxide particles. Carbon atom deposition results from acetylene decomposition at 700 °C. Chen et al (2001) also reported carbon onion formation using radio-frequency plasma CVD reactor. The substrate was composed by cobalt catalyst particles imbibed in silica gel. A CH₄ and H₂ mixture was used as reactant. The reactor chamber was operated at 1 torr, voltage output of 35-50 V and at 573 K.

2.5 Potential Applications and Current Cost of Fullerenes and Nanotubes

Fullerenes and nanotubes are very promising materials for many possible applications due to their interesting properties. Therefore, a brief analysis of the cost and possible industrial applications for fullerenes and nanotubes is in order.
2.5.1 Potential Applications of Fullerenes

According to the reviews carried out by Singh and Srivastava (1995), Da Ros and Prato (2000) and Wilson et al. (2000), the following promising applications for fullerenes can be glimpsed.

C\textsubscript{60} and its derivatives have had strong impact when used in medical therapies. For instance, the above reviews have shown that an excess of oxide radical is the origin of many neurodegenerative diseases. A C\textsubscript{60} derivative (hexa-acid-fullerene) can reduce the neuronal death. In fact, C\textsubscript{60} fullerene has been called a free radical sponge due to its antioxidant properties and high reactivity toward free radicals. Another fullerene derivative, the diamino-diacid-diphenyl-fullerene has exhibited antiviral activity against the HIV virus. This C\textsubscript{60} derivative is almost a perfect fit for the spherical hydrophobic cavity of the HIV protease with a diameter about 10 Å. Once the cavity is occupied by the C\textsubscript{60} derivative the catalytic activity of the virus is inhibited. Fullerenes present also a high antibacterial property. For example, di-tricarbonyl-furan-fullerene has a high antibacterial activity against various species of bacteria and fungal strains including Candida albicans, Bacillus subtilis, Escherichia coli and Mycobacterium avium.

The use of fullerenes as diamond precursor is another important future application. Fullerenes can be transformed in polycrystalline diamond using the non-hydrostatic C\textsubscript{60} compression process at 20 GPa. Hirai et al. (2000) reported that crystalline diamond can be formed if an extreme pressure-temperature combination of about 55 GPa and 3000 K is used.

Pure C\textsubscript{60} can serve as catalyst in petroleum hydrocracking and reforming due to its ability to favour hydrogen transfer reactions. The highly catalytic activity shown by doped fullerenes such as alkali metal fullerenes C\textsubscript{60}M\textsubscript{6} and C\textsubscript{70}M\textsubscript{6} (M = Cs, K, Na) have been used for H\textsubscript{2} – D\textsubscript{2} exchange reactions.

Another important property of alkali doped fullerenes is the ability to act as superconductor. To date, several different doped fullerenes as K\textsubscript{3}C\textsubscript{60} (T\textsubscript{c} = 18 K), Na\textsubscript{2}RbC\textsubscript{60} (T\textsubscript{c} = 2.5 K), Ba\textsubscript{6}C\textsubscript{60} (T\textsubscript{c} = 7 K), Ca\textsubscript{3}C\textsubscript{60} (T\textsubscript{c} = 8.4 K), Rb\textsubscript{3}C\textsubscript{60} (T\textsubscript{c} = 31 K) and RbCs\textsubscript{2}C\textsubscript{60} (T\textsubscript{c} = 33 K) could be used as superconductors. They have shown to efficiently conduct in three dimensions and at the same time, be easy to grow in the form of thin film on substrates. However, alkali doped
fullerenes exhibit superconductive behavior only under inert atmosphere because the metal atoms become oxides if exposed to air.

2.5.2 Potential Applications of Nanotubes

To date, carbon nanotubes have been only used for a small number of commercial applications. Several potential applications, which could become commercialized, were reviewed by Yakobson and Smalley (1997), Subramoney (1998) and Rao et al. (2001). These applications range from mechanical, to electronic and biological fields.

Mechanical applications deal with the mechanical strength of nanotubes. Due to the lightweight (SWCNT density \( \approx 1.33 \, \text{g/cm}^3 \)) and high Young's modulus (\( \sim 1 \, \text{TPa} \)), nanotubes could be used as reinforcement in composite materials. The nanotube's hollow structure gives them remarkably deforming properties as well. For example, nanotubes can be collapsed under a force and will restore their original form once the force is removed. Nanotubes also present a high tensile strength (SWCNT \( \sim 30 \, \text{GPa} \)), which gives them the capacity to resist strong elongation forces. These characteristics make nanotubes the ideal material to built light and strong structures.

One of the most important possible nanotube applications is for use in nanoelectronic device fabrication. Nanotubes are considered an outstanding material for the fabrication of high brightness field-emitters due to their electric transport properties. Choi et al. (1999) reported the fabrication of the first field-emission display. CNTs were vertically aligned using nitrocellulose paste squeeze, surface rubbing and electric field conditioning. The results showed a turn-on field of less than 1 V/\( \mu \text{m} \) and emission currents of 1.5 mA at 3 V/\( \mu \text{m} \) (current density, \( J = 90 \, \mu \text{A/cm}^2 \)). Brightness of 1800 cd/m² at 3.7 V/\( \mu \text{m} \) with fluctuation of around 7% was also observed. An et al. (2001) prepared a supercapacitor using SWCNT electrodes. A maximum specific capacitance of 180 F/g with a power density of 20 kW/kg at an energy density of 7 Wh/kg using a solution of 6.5 N KOH was achieved. Nanotubes have also been studied as a molecular-scale device element. For such an application, it is important to be able to connect the nanotubes between electrodes to built highly integrated electronic devices. Lee et al. (2001b) studied the growth of carbon nanotube nanowiring between nickel
pads. Using a growth barrier technology with chemical vapor deposition straight junction and Y-junction bridges were produced. These bridges act as active components and nanowires in electronic devices at molecular scale.

The possibility of opening the nanotube ends and filling them with other materials has also been studied for some time. Nanotubes can be opened using HNO₃. These open-ended nanotubes could be used as ultrasmall pipettes to penetrate and inject chemical substances into cells with almost no damage. Open-ended nanotubes can be also filled with gold, silver, palladium and platinum for their further use as nanowires.

Owing to the carbon nanotubes present a high chemical stability, large surface and light mass, there has been a considerable interest in studying their use as hydrogen-store material for fuel cell. However, current results regarding hydrogen adsorption in CNTs are extremely scattered from very optimistic to very pessimistic. Wu et al. (2000) performed a hydrogen uptake study by annealed nanotubes at ambient pressure and temperature. They developed an adsorption temperature-depended procedure using a thermogravimetric analyzer. Estimations showed that the sample weight increases by 0.25% while the temperature decreases to room temperature. Rao et al. (2001) reviewed scientific investigations related to the hydrogen adsorption and storage in different crystalline carbon forms at various temperatures and pressures. Overall, SWCNTs were able to storage hydrogen in a range of 4 – 10 wt% (temperature from 80 to 300 K, pressure from 0.04 to 10 MPa), while graphite nanofibers (GNFs) store in a range of 11 – 67 wt% at 11.35 MPa of pressure and room temperature. Reversible electrochemical hydrogen storage process based on hydrogen adsorption, storage and extraction could be applied to secondary hydrogen batteries.

2.5.3 Current Cost of Fullerenes and Nanotubes

Many promising applications exist, however no production technique has been shown economically produce large amounts of fullerenes and nanotubes. The main problem has been the low overall yield and production rate of the continuous CNS synthesis and purification processes. According to Bogdanov et al. (2000) and Churilov (2000), the decline of the fullerene prices after 1994 has been extremely slow as it is shown in Figure 2.18.
Bogdanov also presents an interesting fullerene cost study related with their industrial applications (see Figure 2.19). The cost study shows that even in industries in which fullerenes can become competitive (pharmaceutical, diamond and catalyst), their prices must be decreased by a factor of 10.

![Graph showing price vs year for mixture of fullerenes and pure C60 fullerene](image)

**Figure 2.18**  World Price for (1) Mixture of Fullerenes and (2) Pure C60 Fullerene. Adapted from Bogdanov et al. 2000

Carbon nanotubes are produced mainly by laser ablation, arc vaporization and chemical vapor deposition (CVD). These methods are not economical presenting low production efficiency. Fullerene and nanotube prices reported by several commercial companies including CarboLex, BuckyUSA, NanoLab, and Rosseter Holding vary depending on purity grade, morphology and synthesis methods. Table 2.7 shows the price ranges for different carbon nanotube varieties.

Because the high price, systematic efforts must be devoted in the development of new synthesis methods in order to economically produce larger quantities of carbon nanostructures and decrease their prices.
Figure 2.19  Price for Available Products and Materials in Some Potential Applications for Fullerenes (I) and the Maximum Price for Fullerenes to Be Competitive (II). Adapted from Bogdanov et al. 2000

<table>
<thead>
<tr>
<th>Company</th>
<th>SWCNT AP-Grade $/g</th>
<th>SWCNT HP-Grade $/mg</th>
<th>MWCNT AP-Grade $/g</th>
<th>MWCNT HP-Grade $/mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>CarboLex</td>
<td>60 - 100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BuckyUSA</td>
<td>-</td>
<td>1 - 1.5</td>
<td>100 - 150</td>
<td>-</td>
</tr>
<tr>
<td>NanoLab</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3 - 0.6</td>
</tr>
<tr>
<td>Carbon Solution</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>MER</td>
<td>50 - 80</td>
<td>-</td>
<td>7 - 14</td>
<td>-</td>
</tr>
<tr>
<td>Rosseter Holding</td>
<td>-</td>
<td>-</td>
<td>20 - 30</td>
<td>-</td>
</tr>
<tr>
<td>Carbon Nanotechnologies</td>
<td>-</td>
<td>0.5 - 1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nanoledge</td>
<td>60 - 90</td>
<td>1.4</td>
<td>6 - 10</td>
<td>-</td>
</tr>
</tbody>
</table>

AP-Grade. As prepared grade.

HP-Grade. High purity grade.

- non-available products.

See references list for the company's www site.

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CHAPTER 3    THERMODYNAMIC AND KINETIC STUDY

The equilibrium state is defined as that in which the properties of a system are independent of time. Although this definition considers the equilibrium as a static state, the true equilibrium of a system is a dynamic state in which chemical changes are occurring at molecular level. Hence, at equilibrium, the production rate for any given specie $M_i$ is equal to its destruction rate, i.e. $d(M_i)/dt = 0$ (Benson, 1976). In this context, if the thermodynamic properties of the chemical species involved in the system are known, then it is possible to estimate its final equilibrium composition. The time required to reach the equilibrium state and the chemical species composition during the period of change can be only predicted using basic chemical kinetic principles, which deals with time-depending chemical systems.

Since the equilibrium and conversion rate of a chemical system depend on the temperature, pressure and reactant composition, both must be considered in the study of new chemical processes. For example, most chemical reactions are not carried at equilibrium therefore the reactor design is based on the reaction rate. However, equilibrium considerations must be taken into account in the selection of the operating conditions in order to favour the yield of the desired products.

In this chapter, thermodynamic and kinetic studies are performed. Equilibrium composition of the carbonaceous species is predicted along with the reaction mechanism of the fullerene synthesis.

3.1 Thermodynamic Study of the Fullerene Formation

A thermodynamic study of a reaction system does not allow prediction of the process chemical feasibility for a time-dependant system. It does permit the verification of reactants-products conversions and the process yield. Although the product concentrations calculated by the thermodynamic study may be small, the information's gain from the study allows
establishment of thermodynamic conditions that favour the desired product formation. In a
given process it is not necessary to reach the equilibrium state. The aim of this thermodynamic
study is to determine the operating conditions in which the desired products, fullerenes in our
case, are thermodynamically favoured.

3.1.1 Free Formation Energy ($\Delta G^0_f$) Diagram as Temperature Function for
Different Hydrocarbon Compounds

The Gibbs free energy of formation ($\Delta G^0_f$) is usually used to measure hydrocarbon compound
stability. At given temperature the more stable compounds have the smaller Gibbs free energy.
Thermal stability of hydrocarbon compounds can be studied through the comparison of
formation energies under various temperature conditions. $\Delta G^0_f$ data as temperature function
for various hydrocarbons is presented in Figure 3.1. Note that only light paraffin's such as
CH$_4$, C$_2$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$ are more stables than their basic elements C and H$_2$ at
temperatures lower than 800, 500, 400 and 300 K, respectively.

The relative stability of paraffin's decreases when the number of the carbon atoms in the
molecule increases. This phenomenon can explain the high concentration of light
hydrocarbons and active species such as CH, C$_2$H and CH$_2$ found during the fullerene
synthesis at high temperatures using a hydrocarbon raw material.

Only $\Delta G^0_f$ for acetylene (C$_2$H$_2$) decreases with increased temperature. The $\Delta G^0_f$ value
becomes smaller than other hydrocarbons at temperatures higher than 1800 K. This behavior
explains the high acetylene concentrations found in any hydrocarbon pyrolysis process
operating at temperatures greater than 1500 K.

Figure 3.1 also shows, in general, that the $\Delta G^0_f$ straight line slopes for aromatic compounds
are smaller than those of the paraffinic molecules. This indicates that as the temperature
raises, the thermal stability of the aromatics is larger than the paraffin's. The relative stability
of the aromatic compounds also decreases when the number of aromatic rings in the
hydrocarbon molecule increases. For example, $\Delta G^0_f$ differences with respect to benzene
(C₆H₆) for naphthalene (C₁₀H₈), pyrene (C₁₆H₁₀) and corannulene (C₂₀H₁₀), a fullerene precursor (Pope et al. 1993), are approximately 100, 200 and 400 kJ/mol, respectively.

![Graph showing the relative stability of hydrocarbons as a function of temperature](image)

**Figure 3.1** Relative Stability of Hydrocarbons as Temperature Function

Important observations can be taken from a $\Delta G^0_T$ diagram. However, an equilibrium thermodynamic study on a wide gamma of hydrocarbon compounds is needed to determine if producing fullerenes using hydrocarbons as starting material is realistic.
3.1.2 Chemical Equilibrium of the Reacting Systems

According to Smith et al. (2001), the equilibrium state of a closed system is considered as that in which the system total Gibbs energy is a minimum with respect to all possible changes at a given temperature and pressure. Thus, at equilibrium state,

\[
(dG^f)_{T,P} = 0
\]  

(3.1)

This equation means that, at the equilibrium state for a given temperature and pressure, the total system Gibbs energy remains unchanged even though differential displacements of the chemical reactions occur.

This equilibrium criterion provides a general method for equilibrium state determination. The species concentration of a heterogeneous mixture can be calculated by minimizing total Gibbs free energy of the reacting system at a given temperature. The total Gibbs free energy of a system can be expressed according to the equation 3.2 (Balzhiser et al, 1972).

\[
\frac{G_{mix}}{RT} = \sum_{i=1}^{C} n_i \left( \frac{G_i^o}{RT} + \ln \frac{f_i}{f_i^o} \right) + \sum_{j=1}^{s} n_j \frac{G_j^o}{RT}
\]  

(3.2)

Where \(f_i\) is the partial fugacity for the \(i^{th}\) gaseous specie, \(f_i^o\) is the fugacity for the \(i^{th}\) gaseous specie at the reference state and \(n_i, n_j, G_i^o\) and \(G_j^o\) are the number of moles and the free energy for the \(i^{th}\) gaseous and \(j^{th}\) condensed species. \(c\) and \(s\) are the total number of gaseous and condensed species. \(R\) is the gas constant and \(T\) the absolute temperature. The first term of the right hand of the equation corresponds to the gaseous species contribution. The second term corresponds to the contribution of condensed species, which are assumed to be mutually insoluble.
Under the low pressure and high temperatures found in plasma, the ideal gas conditions can be assumed in such a way that,

\[
\frac{f_i}{f_i^o} = \frac{n_i}{n} \quad (3.3)
\]

Where \( n \) is the sum of the number of moles for all gases. Thus, equation 3.2 becomes,

\[
\frac{G_{\text{mix}}}{RT} = \sum_{i=1}^{c} n_i \left( \frac{G_{i}^o}{RT} + \ln \frac{n_i}{n} \right) + \sum_{j=1}^{c} n_j \frac{G_{j}^o}{RT} \quad (3.4)
\]

In the equation 3.4, \( n_i \) is constrained by the atomic species conservation. Therefore, \( n_i \) must satisfy the relation:

\[
\sum_{i=1}^{c} a_{ki} n_i = b_k \quad \text{for} \quad 1 \leq k \leq M \quad (3.5)
\]

Where \( a_{ki} \) are the number of gram-atoms for the \( k^{th} \) element in a mole of the \( i^{th} \) specie and \( M \) is the number of elements present in the reacting mixture.

The mixture composition, which corresponds to the minimum of the total Gibbs free energy function, is found using the method of steepest descent, first developed by White et al. (1958).

In our case, the thermodynamic computations were performed using the computer software FACTSAGE version 5.0, which was developed by the Center for Research in Computational
Thermochemistry of the Ecole Polytechnique at the Université de Montréal in collaboration with GTT-Technologies, GmbH, Aachen, Germany.

Two reacting systems were thermodynamically analyzed. The type of raw material and catalyst used during the experimental part were accounted in the computations. The first reacting system involved the use of acetylene (C$_2$H$_2$) as starting material, iron (Fe) was used as catalyst and argon-helium (Ar)-(He) mixture was used as plasma gas. The second system involved carbon black (C$_s$) as starting material, iron (Fe) or nickel (Ni) as catalyst and the same plasma gas mixture. The complete compound lists for both reacting systems are shown in attachments 1 and 2.

**a) Chemical Equilibrium for the Carbon-Hydrogen System**

The thermodynamic computation results for the carbon-hydrogen system are shown in Figures 3.2, 3.3, 3.4 and 3.5. These figures detail molar mass evolution as function of temperature. The initial reactant mixture consisted of 0.4 moles of C$_2$H$_2$, 0.04 moles of Fe, 1 mol of Ar and 5 moles of He at a constant pressure of 101.15 kPa.

It is important to remark that different scales on the molar mass axis have been used for the figures. These changes allowed scanning all the possible hydrocarbon compounds that might be involved during the synthesis of fullerenes.

The analysis of the equilibrium diagrams can be performed considering different temperature zones.

The first zone, from 500 to 1500 K (see Figure 3.2 and 3.3), is characterized by the iron catalyst vaporization and the presence of short chains hydrogen-rich molecules such as CH$_4$, C$_2$H$_2$, C$_2$H$_4$ and C$_2$H$_6$.

The molar concentration of long chain saturated hydrocarbons such as C$_3$H$_8$, C$_4$H$_{10}$, C$_5$H$_{12}$ and C$_6$H$_{14}$ is quite small due the easy thermal breakup of the C - C bonds. Bond thermal stability decreases with the hydrocarbon chain length.
Figure 3.2 Overall Diagram of the Chemical Equilibrium for the Carbon-Hydrogen-Iron System.

$0.4 \text{C}_2\text{H}_2 + 0.04 \text{Fe} + \text{Ar} + 5 \text{He}, P = 101.15 \text{kPa}$
The second zone, from 1500 to 3000 K, is characterized by the high thermal breakup of the C–C bonds and the formation of molecules with triple C–C bonds. These triple bonded molecules are considered carbon black precursors. Acetylene and radical species concentrations such as H, CH, C₂H and C₃H begin to become significant. There is also a corresponding decrease in hydrogen-rich molecules. This temperature range also favours the Fe₃C formation produced by the reaction between the carbonaceous species and the iron catalyst. This result suggests that metal fullerene formation may be possible during the plasma treatment.

![Graph showing the thermodynamic behavior of paraffin's and olefins.](image)

Figure 3.3 Thermodynamic Behavior of Paraffin's and Olefins.
0.4 C₂H₂ + 0.04 Fe + Ar + 5 He, P =101.15 kPa
The third zone, which includes temperatures further on 3000 K, is characterized by a high yield of gas carbon species and radical hydrogen. These species have been produced by the breakup of the last C – C and C – H bonds.

At equilibrium, Figure 3.4 shows that aromatic compounds with small number of rings such as C_6H_6, C_{10}H_8, C_{14}H_{10} and C_{16}H_{10} might be formed over a wide temperature range of 1000 to 3000 K. Their molar fraction would be much smaller than those of the active species also found in the same temperature range. The molar mass of the aromatic hydrocarbons decreases and the formation temperature range narrowed when the number of aromatic rings in the molecule increase. For example, the molar mass for C_{30}H_{10}, C_{40}H_{10}, C_{50}H_{10} and C_{60}H_{10} are so small that they can be considered negligible.

Figure 3.4  Thermodynamic Behavior of Aromatic Molecules and Fullerenes.

0.4 C_2H_2 + 0.04 Fe + Ar + 5 He, P = 101.15 kPa
The equilibrium diagram for the carbonaceous species depicted in the Figure 3.5 shows that solid carbon is formed from 500 to 3000 K. Fullerenes are formed in the temperature range from 2250 to 3800 K. Figure 3.5 shows the highest molar concentration of fullerenes at approximately 3500 K. High molar concentrations of the C₂ and C₃ species, which are considered fullerene precursors, are also observed at temperatures higher than 2500 K. These results confirm that a high carbon black production would be expected during the pyrolysis of C₂H₂ below 3000 K. It is likely that C₂ and C₃ species and fullerenes would be favoured in the plasma reactor since the plasma temperatures are typically above 2500 K (Chang and Pfender, 1987).

![Figure 3.5 Thermodynamic Behavior of Carbon and Iron Species and Fullerenes.](image)

0.4 C₂H₂ + 0.04 Fe + Ar + 5 He, P = 101.15 kPa
The concentrations of atomic hydrogen and small hydrocarbon radicals such as CH, CH₂ and C₂H will also be abundant at temperatures higher than 2500 K. In these conditions, the hydrogen and the small hydrocarbon radicals become competition species for the C₂ and C₃ molecules. They will decrease the carbon vapor pressure inside the plasma reactor and inhibit the fullerene growth.

The use of acetylene as carbon source for fullerene production seems to favour the synthesis of carbon black with small hydrocarbon chains as by-products rather than fullerenes and related carbon nanostructures.

\textit{b) Chemical Equilibrium for the Solid Carbon Vaporization}

Since hydrogen atoms present in the hydrocarbon molecules prevent the fullerene formation, carbon black was considered as raw material. The use of carbon black as raw material will increase the carbon vapor pressure in the plasma reactor while eliminating the hydrogen-content radical species formation.

Two reaction systems were considered during the chemical equilibrium study. The first reaction system involves carbon black as raw material source, Argon (Ar) and Helium (He) as plasma gas and iron (Fe) as catalyst. The second involves the same raw material and plasma gas but nickel (Ni) instead of iron was used as catalyst.

The influence of the initial carbon black concentration and the reactor pressure on fullerene equilibrium concentration was also analyzed.

Figure 3.6 and 3.7 show the chemical equilibrium for the two reaction systems at total pressure of 101.15 kPa. In both systems, solid carbon is stable at temperatures lower than 3000 K. The vaporization of solid carbon is reached at temperatures about 3250 K. The iron and nickel catalysts are stable at temperatures lower than 1250 and 2250 K, respectively.

These results suggest that at plasma temperatures (above 2500 K), the fullerene growth is best carried out under homogenous reaction conditions. All species present in the plasma should be in gas-phase.
As expected, the formation temperature for fullerenes ranges from 2250 to 3800 K. The highest fullerene concentration is reached at 3500 K. This temperature range also corresponds to higher production of precursor species including C₂ and C₃ and small carbon clusters such as C₄, C₅, C₆, C₇, C₈, C₉ and C₁₀. The results also show that the molar mass of carbon clusters decreased while the carbon chain growths. In this way, the equilibrium molar concentration of fullerenes is extremely small and may be considered negligible.
Thermodynamic results suggest that fullerene growth is extremely difficult to achieve when considering only plasma thermal effects.

Figure 3.6 shows the high stability of the iron carbide (Fe$_3$C) in the temperature range from 1200 to 2200 K. Taking into account the prevailing temperatures in the plasma reactor and the quenching system, this result suggests that metal fullerene formation may be also quite possible.

Figure 3.8 shows the effect of the initial carbon concentration on the carbonaceous species composition at the equilibrium state. Upon comparison with Figure 3.7, it is evident that a higher carbon molar concentration does not strongly influence the height of the carbon species and fullerene curves at equilibrium. The molar concentration of the different carbon species
and fullerenes remains unaffected. The additional initial carbon slightly increases the temperature range in which the fullerene formation is carried out. In this case, the gamma of stability temperatures for the fullerenes ranges from 2250 to 4000 K (Figure 3.8) rather than from 2250 to 3800 K (Figure 3.7).

![Chemical Equilibrium](image)

Figure 3.8   Chemical Equilibrium for the System: C + 0.003 Ni + Ar + 5 He, 
P = 101.15 kPa

Additionally, the total pressure effect on the chemical equilibrium of the reacting system was also studied. Figure 3.9 depicts the chemical equilibrium study performed under vacuum pressure conditions of 50.5 kPa. Figure 3.10 shows the effect on chemical equilibrium composition above atmospheric pressure at 505.75 kPa.
Figure 3.9 shows how the use of a vacuum inside the plasma reactor affects the fullerene formation. The equilibrium concentrations of fullerenes are decreased. In contrast, the formation of small carbon clusters such as C$_2$ and C$_3$ are favoured. At 50.5 kPa the highest fullerene concentration is reached at a temperature about 3000 K. This is 500 K lower than that found at atmospheric pressure.

Vacuum operating condition also slightly narrows the temperature range in which the fullerene formation proceeds.

These results clearly indicate that a vacuum pressure in the reacting system disrupts fullerene growth. At best, amorphous carbon or graphitic structures are favoured under vacuum.

Figure 3.9  Chemical Equilibrium for the System: 0.4 C+ 0.003 Ni + Ar + 5 He,
P = 50.5 kPa
The increase of the system pressure above atmospheric slightly favours fullerene equilibrium concentration. The improved fullerene production is due to a reduction of the equilibrium concentration of the small carbon clusters (see Figure 3.10). A high system pressure also increases the temperature range for fullerene formation. At 505.8 kPa fullerenes were produced from 2300 to 4200 K.

This large temperature range for fullerene formation at high system pressure strongly favours the fullerene synthesis under thermal plasma conditions. Thermal plasma temperatures are on the order of 10,000 K at the plasma jet center.

Figure 3.10  Chemical Equilibrium for the System: 0.4 C + 0.003 Ni + Ar + 5 He, 
P = 505.8 kPa
It is important to remark that at high system pressure, the solid carbon also becomes stable in a larger temperature range. At high pressure, complete solid carbon vaporization is reached at approximately 3750 K instead of 3250 K under atmospheric conditions. Particle residence time in RF induction plasma is about 20 ms (Boulos, 1991) therefore complete carbon black particle vaporization seems to be a difficult problem.

Finally, the fullerene concentrations found in the various studies on chemical equilibrium are significantly smaller than those reported in the literature using other procedures (Huczko et al. 1995, Cota et al. 2001). This difference suggests that the formation of fullerenes and related nanostructures under high thermal conditions must be kinetically controlled rather than thermodynamically.

3.2 Kinetic Study of the Fullerene Formation

The kinetic study of any reacting system provides information regarding the reaction rates of chemical species, the influence of the operating parameters on the reaction rates and the detailed reaction mechanism.

The objective of this kinetic study is to better understand the kinetic behavior of the chemical species involved in the reaction mechanism of fullerene formation at temperatures greater than 2000 K. A theoretical kinetic simulation capable of reproducing the experimental results would be outstanding. However, that simulation work is beyond the overall objectives of this chapter.

According to Kee et al. (1996), the elementary reversible reactions \( I \) involving \( K \) chemical species can be represented by the general form

\[
\sum_{k=1}^{K} v_{ki} X_k \leftrightarrow \sum_{k=1}^{K} v_{ki}^r X_k \quad \quad (i = 1, \ldots, I)
\]  

(3.6)
Where $X_k$ is the chemical symbol for the $k^{th}$ species, and $v'_{ki}$ and $v''_{ki}$ are the forward and reverse stoichiometric coefficients, respectively.

The mathematical model of this kinetic system produces $K$ differential equations, which represent the production or consumption of the $k^{th}$ chemical species as a time function. This system is represented by the overall equation

$$
\frac{d[X_k]}{dt} = \sum_{i=1}^{I} v_{ki} \left\{ k_{fi} \prod_{k=1}^{K} [X_k]^{v_{ki}} - k_{ri} \prod_{k=1}^{K} [X_k]^{v_{ki}} \right\}
$$

(3.7)

With

$$
v_{ki} = v''_{ki} - v'_{ki}
$$

(3.8)

Where $[X_k]$ is the molar concentration for the $k^{th}$ chemical species and $k_{fi}$ and $k_{ri}$ are the forward and reverse rate constants for the $i^{th}$ reaction, respectively.

The forward rate constants are assumed to have the Arrhenius temperature dependence, according to the equation

$$
k_{fi} = A_i T^{\beta_i} \exp \left( -\frac{E_i}{RT} \right)
$$

(3.9)

Where $A_i$ is the pre-exponential factor, $\beta_i$ the temperature exponent and $E_i$ the activation energy for the $i^{th}$ reaction.
Additionally, the reverse rate constants are calculated using the equilibrium constant as

\[ K_{ci} = \frac{k_{fi}}{k_{ri}} \]  

(3.10)

Where \( K_{ci} \) is the equilibrium constant for the \( i^{th} \) reaction.

The kinetic system with \( K \) differential equations was resolved using the Chemical Kinetic Simulator computer software, version 1.0 (IBM Co., 1995). This routine was initially developed by Gillespie (1977). It finds a solution using a *stochastic simulation method* in which the changes in the system are modeled by randomly selecting among probability-weighted reaction steps.

### 3.2.1 Reaction Mechanism for the Growth of Fullerenes and Planar Graphitic Structures using Solid Carbon as Starting Material

The chemical kinetic study was performed to analyze the evolution through time of fullerene precursors, fullerenes and planar graphitic structures under thermal plasma conditions. The chemical kinetic mechanism included the following steps: solid carbon vaporization, the formation of fullerene precursors as \( \text{C}_2 \) and \( \text{C}_3 \), carbon nuclei growth and the nuclei transformation into planar graphitic structures or fullerenes. Table 3.1 shows the elementary reactions involved in reaction mechanism and the kinetic parameters for the rate constants (\( k \)) according to the Arrhenius expression. Here, \( k \) is expressed in cm\(^3\)/mol s and \( E \) in kJ/mol.

For a given reaction, all the kinetic parameters were taken from the references shown in the right column of the Table 3.1 or were calculated using the equilibrium constant values. Additionally, the kinetic parameters for the reaction \( \text{C}_2 + \text{C}_2 = \text{C}_n \) were considered being those of the reaction \( \text{C}_2 + \text{C}_2 = \text{C}_4 \), while the kinetic parameters of the reaction \( \text{C}_3 + \text{C}_3 = \text{C}_6 \) were used for the reaction \( \text{C}_3 + \text{C}_3 = \text{C}_m \).
Table 3.2 shows the thermochemical data used during the computations such as the formation enthalpy (\(\Delta H_f\)) at 298.15 K and the specific heat (\(C_p\)) coefficients, which were expressed according to the equation 3.11.

\[
C_p = a_1 + a_2 T + a_3 T^2 + a_4 T^3
\]  

(3.11)

**TABLE 3.1  KINETIC PARAMETERS OF THE REACTIONS INVOLVED IN THE GROWTH MECHANISM OF FULLERENES**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(A)</th>
<th>(\beta)</th>
<th>(E)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid Carbon Vaporization</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs = C</td>
<td>3.70 \times 10^5</td>
<td>0.00</td>
<td>73.7</td>
<td>a</td>
</tr>
<tr>
<td><strong>C₂ Precursor Formation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C + C + M = C₂ + M</td>
<td>3.10 \times 10^7</td>
<td>-1.50</td>
<td>-460.2</td>
<td>b</td>
</tr>
<tr>
<td>C + C = C₂</td>
<td>5.20 \times 10^{10}</td>
<td>-0.50</td>
<td>25.5</td>
<td>b</td>
</tr>
<tr>
<td><strong>C₃ Precursor Formation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂ + C = C₃</td>
<td>1.28 \times 10^{13}</td>
<td>-1.24</td>
<td>2.4</td>
<td>b</td>
</tr>
<tr>
<td>C₂ + C₂ = C₃ + C</td>
<td>2.50 \times 10^{14}</td>
<td>0.00</td>
<td>74.9</td>
<td>b</td>
</tr>
<tr>
<td><strong>Growth of the Nuclei Via C₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂ + C₂ = Cn</td>
<td>6.62 \times 10^4</td>
<td>0.64</td>
<td>-135.7</td>
<td>b</td>
</tr>
<tr>
<td>C₂ + Cn = Cn</td>
<td>4.50 \times 10^{12}</td>
<td>0.50</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td>C₂ + Cm = Cm</td>
<td>4.50 \times 10^{12}</td>
<td>0.50</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td><strong>Growth of the Nuclei Via C₃</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃ + C₃ = Cm</td>
<td>3.16 \times 10^4</td>
<td>0.00</td>
<td>-88.3</td>
<td>b</td>
</tr>
<tr>
<td>C₃ + Cm = Cm</td>
<td>4.50 \times 10^{12}</td>
<td>0.50</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td>C₃ + Cn = Cn</td>
<td>4.50 \times 10^{12}</td>
<td>0.50</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td><strong>Transformation of the Nuclei into Planar Graphitic Structures</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cn = Sn</td>
<td>1.00 \times 10^6</td>
<td>0.00</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td>Cm = Sm</td>
<td>1.00 \times 10^6</td>
<td>0.00</td>
<td>0.0</td>
<td>b</td>
</tr>
<tr>
<td><strong>Transformation of the Nuclei into Fullerenes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cn = Fn</td>
<td>3.00 \times 10^{13}</td>
<td>0.00</td>
<td>300.0</td>
<td>b</td>
</tr>
<tr>
<td>Cm = Fm</td>
<td>3.00 \times 10^{13}</td>
<td>0.00</td>
<td>300.0</td>
<td>b</td>
</tr>
</tbody>
</table>

- a - Smith and Smooth, 1980.

The effects of two operating parameters on the kinetic behavior of reacting system were studied. The first was the effect of the molar ratio between the solid carbon and the plasma
gas. Ratios of 0.05 and 0.25 were used to simulate high dilution and high carbon concentration conditions, respectively. The second effect was that of the temperature at which the reaction proceeds. Three different simulations were carried out at constant temperature of 2000, 2500 and 3000K. In all simulations helium was the plasma gas, which acted as the third body (M).

### TABLE 3.2 FORMATION ENTHALPY ($\Delta H_f$) AND Cp COEFFICIENTS FOR THE SPECIES INVOLVED IN THE CHEMICAL KINETICS

<table>
<thead>
<tr>
<th>Specie</th>
<th>$\Delta H_f$ (kJ/mol)</th>
<th>$a_1$ (J/mol)</th>
<th>$a_2, X 10^{4}$ (J/mol K)</th>
<th>$a_3, X 10^{7}$ (J/mol K²)</th>
<th>$a_4, X 10^{11}$ (J/mol K³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>716.67</td>
<td>21.09</td>
<td>-7.69</td>
<td>4.50</td>
<td>-4.47</td>
</tr>
<tr>
<td>C₂</td>
<td>837.74</td>
<td>32.17</td>
<td>41.90</td>
<td>-5.32</td>
<td>3.84</td>
</tr>
<tr>
<td>C₃</td>
<td>820.06</td>
<td>31.80</td>
<td>170.00</td>
<td>-47.90</td>
<td>36.20</td>
</tr>
<tr>
<td>C₄</td>
<td>1225.91</td>
<td>152.91</td>
<td>-1745.00</td>
<td>1450.00</td>
<td>-3180.00</td>
</tr>
<tr>
<td>C₅</td>
<td>970.69</td>
<td>43.72</td>
<td>420.00</td>
<td>-134.00</td>
<td>135.00</td>
</tr>
<tr>
<td>C₆</td>
<td>1.89</td>
<td>5.51</td>
<td>201.00</td>
<td>-62.60</td>
<td>64.20</td>
</tr>
<tr>
<td>Fm</td>
<td>2755.00</td>
<td>357.79</td>
<td>14400.00</td>
<td>-4820.00</td>
<td>5080.00</td>
</tr>
<tr>
<td>Fn</td>
<td>2530.00</td>
<td>302.21</td>
<td>12300.00</td>
<td>-4120.00</td>
<td>4360.00</td>
</tr>
<tr>
<td>M</td>
<td>0.0</td>
<td>0.0</td>
<td>200000.00</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Sm</td>
<td>716.67</td>
<td>21.09</td>
<td>-7.69</td>
<td>4.50</td>
<td>-4.47</td>
</tr>
<tr>
<td>Sn</td>
<td>716.67</td>
<td>21.09</td>
<td>-7.69</td>
<td>4.50</td>
<td>-4.47</td>
</tr>
</tbody>
</table>

#### 3.2.2 Effect of the Solid Carbon-Gas Initial Molar Ratio on the Reacting System Kinetics

The initial molar ratio between the solid carbon and the plasma gas (He) was varied. The goal was to evaluate the influence of a high inert plasma gas concentration and a high initial carbon concentration on the chemical kinetics during the fullerene growth.

The kinetic behavior of the carbon species considering a reacting system under conditions of high dilution by the plasma gas is depicted in Figure 3.11. The kinetic behavior under high initial carbon concentration is shown Figure 3.12. In these cases, a carbon solid-inert gas molar ratio of 0.05 and 0.25 were used.

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Figure 3.11 and 3.12 show that solid carbon vaporization is reached approximately $1 \times 10^{-3}$ s under both conditions. The variation of the initial conditions clearly affects the molar concentration of the C, C$_2$ and C$_3$ species, fullerenes (Fn) and planar graphitic structures (Sn) produced via C$_2$ precursors.

![Graph showing chemical kinetics of carbon species](image)

**Figure 3.11** Chemical Kinetics of Carbon Species during the Fullerene Growth at High Dilution Conditions. Initial Conditions: $2 \times 10^{-6}$ mol Cs + $4 \times 10^{-5}$ mol He, $T=2500$ K

The reaction rate of the C compound is sped-up when a high solid carbon concentration is used as starting material. For example, when a high solid carbon concentration is used, the C compound formation begins about $1 \times 10^{-9}$ s instead of $1 \times 10^{-8}$ s for high inert gas dilution. As a consequence, the C$_2$, Sn and Fn concentrations are also increased and their respective reaction rates are sped-up. The formation of fullerene and graphitic structures via C$_2$ precursor is enhanced under high carbon concentration conditions.
3.2.3 Temperature Effect on the Reacting System Kinetics

Three simulations at different temperatures were performed to determine the temperature effect on the reacting system kinetics.

Figure 3.12 Chemical Kinetics of Carbon Species during the Fullerene Growth at High Solid Carbon Concentration. Initial Conditions: \(1 \times 10^{-5}\) mol Cs + \(4 \times 10^{-5}\) mol He, T=2500 K

Figure 3.11 shows the results using a reaction temperature of 2500 K. Figure 3.13 and 3.14 show the kinetic simulation results at 2000 and 3000 K, respectively.

A general comparison of the three studies shows that a higher reaction temperature clearly speeds up the reaction rate. The C compound formation begins about \(1 \times 10^{-8}\) s for 2000 K (Figure 3.13), about \(8 \times 10^{-9}\) s for 2500 K (Figure 3.11), and \(6 \times 10^{-9}\) s for 3000 K (Figure 3.14).
An increase in the reaction temperature strongly enhances the yield of carbon species $C$ and $C_3$. These species in turn favour fullerene formation (Fm) via the sequential additions of $C_3$ precursors. The molar concentration of the $C_2$ species remains almost unchanged despite increasing reaction temperature. As a result, the fullerene concentration (Fn) produced via the sequential addition of $C_2$ precursors is only slightly lower.

![Graph showing chemical kinetics of carbon species during fullerene growth at 2000 K.](image)

**Figure 3.13** Chemical Kinetics of Carbon Species during the Fullerene Growth at 2000 K. Initial Conditions: $2 \times 10^6$ mol Cs + $4 \times 10^5$ mol He

The increasing of reaction temperature has a remarkably effect on the formation of planar graphitic structures via the addition of $C_2$ and $C_3$ precursors. At higher temperatures, the concentration of graphitic structures (Sn and Sm) tends to decrease and promotes formation of amorphous rather than graphitic carbon.
Figure 3.14  Chemical Kinetics of Carbon Species during the Fullerene Growth at 3000 K. Initial Conditions: $2 \times 10^{-6}$ mol Cs + $4 \times 10^{-8}$ mol He

A plot of the evolution of the molar concentration versus the reaction temperature is shown in Figure 3.15. Taking into account the reaction times to reach the equilibrium at the different temperatures, a reaction time of $1.5 \times 10^{-2}$ s was used to carry out this analysis.

Based on Figure 3.15 an increase of the reaction temperature favours the fullerene formation via the sequential addition of C$_2$ and C$_3$ precursors. Above 2500 K, the fullerene yield is strongly enhanced through the Fm formation (using C$_3$ precursors) rather than Fn formation (using C$_2$ precursors). At the same time, high reaction temperatures prevent the formation of planar graphitic structures (Sn and Sm).

The results show the use of high reaction temperatures favour the fullerene formation, and prevent the formation of graphitic structures. However, it is important to remark that under these conditions the formation of C and C$_3$ species are also favoured. As a consequence a high amorphous carbon yield will also be produced. A temperature in the range from 2500 to
2800K is proposed as the optimal operating temperature. At these temperatures the formation of fullerenes is favoured while amorphous carbon yield is minimized.

Figure 3.15  Temperature Effect on the Chemical Kinetics of Carbon Species during the Fullerene Growth. Initial Conditions: 2 X 10^{-6} mol Cs + 4 X 10^{-5} mol He, t=1.5X10^{-2} s

The results obtained in the chemical kinetic study for C and C_2 and C_3 concentrations completely agree with those obtained in the thermodynamic equilibrium study (paragraph 3.1.2). In other words, similar molar concentrations for the carbon species C, C_2 and C_3 are found at the equilibrium in both studies (see also Figure 3.8).

It is reasonable to assume the kinetic mechanism using the sequential additions of the fullerene precursors C_2 and C_3 strongly represents the carbon growth pattern of fullerenes at high temperatures.
CHAPTER 4 \hspace{1cm} EXPERIMENTAL SET-UP, PROCEDURES AND CHARACTERIZATION TECHNIQUES.

Taking into account the performance of the different plasma systems shown in Chapter 1, a new method to produce carbon nanostructures CNSs (fullerenes and nanotubes) is proposed. The method is based on the evaporation of carbon and catalyst particles using a radio frequency (RF) inductively coupled plasma torch. This source of energy will be used to activate the precursor species of CNSs.

This chapter describes the experimental equipment and statistical experimental design developed to perform the CNS synthesis. In addition, the analytical techniques used to characterize the carbon vaporization and the solid products are also discussed.

4.1 Experimental Equipment

According to the bibliographic review on plasma systems in the Chapter 1, the RF induction plasma approach appears to be one of the most promising technologies for CNS production. One of the most interesting aspects of RF plasma is the long residence time in zones where the precursor-initiating or CNS coalescence phenomena is important.

The CNS synthesis method is based on the carbon and catalyst particle evaporation using a RF plasma reactor. Some of the most significant chemical and physical phenomena involved in the method’s ability to more efficiently synthesize CNSs are related to: 1) the production and interaction of the carbon vapor and the metal vapor catalyst generated into the plasma, 2) the chemical and physical evolution of the carbon and catalyst species into the reactor, and 3) the different reactor zones, which are characterized by specific residence times throughout the different temperature gradients.

The RF plasma system also has the ability to control the vaporization process of carbon and catalyst. The autonomy of the system is made possible by varying the operating parameters
such as, the electrical power, the reactor pressure, the carbon and catalyst feed rate, the carbon-catalyst percent ratio, and the type of plasma gas.

4.1.1 Experimental Set-Up

All the experimental tests were carried out according to the experimental setup shown in Figure 4.1. The experimental equipment used was separated in two sections for practical and technical purposes. One section included the R.F induction plasma torch used to vaporize the mixture of reactants, the reactor (150-mm i.d., 500-mm long) and the quenching zone (130-mm i.d., 500-mm long). In this section, the reactor and the quenching were constructed in stainless steel with a water-cooled jacket for carbon vapor condensation. The reactor and the quenching included a series of type K thermocouples to evaluate the temperature zones during the experimentation.

![Figure 4.1 Experimental Setup of the Production Process of Carbon Nanostructures](image-url)
The second section included the filtration system. This system was comprised of three stainless steel filters (60-mm o.d., 457-mm long, rated at 2.8 μm in gas service) to separate the solid product (soot) before exhausting the gas to the vacuum pump.

After each experimental test, the soot was collected at the bottom of the system and characterized using various analytic techniques.

The reactor design allowed the incorporation of an in-situ emission spectroscopy device to evaluate the effect of operating parameters on the vaporization process of the carbon-catalyst mixture.

4.1.2 Plasma Source

The R.F. power supply used during the experimental part was a Lepel 60 kW unit working with an oscillator frequency from 2 to 5 MHz.

![Diagram of R.F. Inductively Coupled Plasma Torch TEKNA PL-50](image)

Figure 4.2 R.F. Inductively Coupled Plasma Torch TEKNA PL-50
A Tekna PL-50 induction plasma torch (see Figure 4.2) with a quartz confinement tube of 50-mm i.d. and 4-turn coil was used to vaporize the mixtures of reactants. The flow rates of the different plasma gas applied in all the experimental tests were maintained constants as shown in Table 4.1.

<table>
<thead>
<tr>
<th>Plasma Gas</th>
<th>Type of Gas</th>
<th>Gas Flow Rate (slpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central</td>
<td>Argon</td>
<td>30</td>
</tr>
<tr>
<td>Sheath</td>
<td>Helium</td>
<td>120</td>
</tr>
<tr>
<td>Powder</td>
<td>Helium</td>
<td>6 - 10</td>
</tr>
</tbody>
</table>

The reactant mixture composed primarily of carbon black and catalyst powder was fed using a Sylco MARK IX (serial 579) powder feeder. The powder feeder was operated using two different screws. A screw with a pitch of 10 steps/inch was used in the experimental tests performed at lower feed rates, while a screw pitch of 7 steps/inch was utilized in those tests in which a higher feed rate was used. The reactant mixture was axially introduced through a water-cooled probe localized at the center of the plasma torch.

4.2 Operating Conditions

Two test series were performed during the experimental part of this study. The first series was used as preliminary tests. Sources of carbonaceous starting material were acetylene, carbon black and tetrachloroethylene. Iron, nickel and cobalt were used as catalysts. Regarding the results obtained in the preliminary tests, in the second testing series the raw materials used were mixtures of carbon black and nickel powders.
4.2.1 Preliminary Experimental Tests

Before performing a complete statistical experimental design, a series of preliminary experiments were carried out to determine the method's ability to synthesize CNSs. Three different carbonaceous materials were used as raw materials. The first, acetylene (C$_2$H$_2$), was used to evaluate the influence of a hydrogen-rich reacting atmosphere on the CNS synthesis. The second was carbon black powder (BP-3700, Cabot Co.) as starting material. It was used to evaluate the CNS production in a hydrogen-free and high carbon concentration atmosphere. In an attempt to improve the vaporization by using a liquid raw material, the third material tested was tetrachloroethylene (C$_2$Cl$_4$). Various metal powders such as iron (Fe, 98%, 14 +/- 7 μm), nickel (Ni, 99.8%, -325 mesh) and cobalt (Co, 99.8%, -325 mesh) were evaluated as catalyst.

Both constant and variable parameters were considered when acetylene and carbon black were used as starting materials. Among the constant parameters were plate power of 40 kW, reactor pressure of 66 kPa (500 torr) and the powder, central, and sheath gas flow rates indicated in Table 4.1. The variable parameters were the source of starting material (acetylene and carbon black), the type of catalyst (Fe, Co-Ni), and the raw material-catalyst ratio.

The test carried out using C$_2$Cl$_4$ as raw material was performed at 79 kPa (600 torr) of reactor pressure, 30 kW of plate power with flow rates of 40 slpm of sheath, 120 slpm of central, and 8 slpm of powder.

Preliminary tests showed that when acetylene was used as raw material, the produced soot was mainly composed of amorphous carbon. Only fullerene traces were synthesized. In contrast, carbon black and C$_2$Cl$_4$ both showed higher fullerene yield. Due to the highly dense chlorine atmosphere produced during the experiment with C$_2$Cl$_4$, all tests with this compound were abandoned for technical and safety reasons as it will be shown later in Chapter 5.

The complete results of the preliminary tests shall be described in detail in Chapter 5. In this section, the overall results are presented in order to provide a technical foundation for the development of the experimental statistical design.
4.2.2 Statistical Experimental Design

Experimental design methods play an important role in most of the researching activities in which it is important to study the combined effect of several parameters on a response variable. A statistical experimental design was developed to study the influence of operating parameters on the fullerene yield. A factorial plan with four factors and two levels was designed with the \( C_{60} \) yield as the response variable. The four factor involved in the experimental plan were the generator plate power, the reactor pressure, the carbon black-catalyst ratio and the raw material feed rate. Based on the results of preliminary tests, it was evident that the highest fullerene production occurred when carbon black was used as the starting material. Therefore, carbon black (BP 3700) and nickel powder (Ni, 99.8%, -325 mesh) were used as carbonaceous starting material and catalysts. Both powders were mixed using two different nickel molar concentrations to evaluate the effect of the catalyst. Table 4.2 summarizes the \( 2^4 \) factorial design including the low and high-level values used for each factor.

During these experiments, the flow rates of the plasma gases were maintained constant as shown in Table 4.1.

TABLE 4.2 \( 2^4 \) STATISTICAL FACTORIAL DESIGN

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coded Factor</th>
<th>Low Level</th>
<th>High Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Pressure, kPa</td>
<td>A</td>
<td>40</td>
<td>66</td>
</tr>
<tr>
<td>Mixture Feed Rate, g/min</td>
<td>B</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Carbon Black-Catalyst Ratio, %mol</td>
<td>C</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Plate Power, kW</td>
<td>D</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

4.3 Characterization Techniques

Fullerenes and nanotubes are uncommon materials. Many efforts must be devoted on their characterization in order to completely understand their properties and formation mechanisms.
The use of characterization techniques in the synthesis process is needed. In this work, the following techniques were used to analyze the CNS synthesized.

4.3.1 Laser Droplet Size Analyzer

Because carbon black and nickel mixture tends to agglomerate, large particles of raw material agglomerates are observed. A droplet size analyzer was used to determine the mean diameter and the size distribution of the carbon black-nickel agglomerates. The measuring equipment is shown in the Figure 4.3. It consists of a powder feeder, a pressurized carried air-line, an injection probe and a particle size measurement instrument.

Figure 4.3 Experimental Set Up of the Droplet Size Analyzer
The technical procedure involved the following steps: first, the powder was weighted and placed in the powder feeder, then the air stream, from a high-pressure air line, was introduced to the powder feeder through a pressure regulator and a flowmeter. The air was used to carry the carbon particles to the injection probe. The probe was vertically oriented into the measuring instrument, injecting the powder into an open environment.

The laser droplet size analyzer was a Malvern/Insitec Ensemble Particle Concentration and Sizes Instrument System. This system measures the particle size distribution via light scattering. In principle, the particles placed in the path of a helium-neon laser beam (5mW, 600 nm) diffract the light in the beam as a function of their particle size or cross-sectional area. The total amount of diffracted light from the particles is received onto a series of concentric, radial; photodiode detector. The amount of laser light received depends on both the sizes and the volume of particles. The analysis of the detectors’ output yields a size distribution by volume, from which a mean size can be derived.

Figure 4.4  Particle Size Distribution of the Carbon Black-Nickel Mixture
The instrument was calibrated using air with a refractive index of \(1.0 + 0.0i\). A refractive index of \(2.5 + 0.5i\) was used for the mixture of carbon black-nickel powders. According to the EPCS Technical Specification, the instrument measuring error was estimated to be better than \(\pm 2\%\) with accuracy over 96\% of the particle size distribution.

Figure 4.4 depicts a typical particle distribution of the powder mixture using a flow rate of 2 g/min and 8 slpm for the mixture and the carried gas, respectively. The blue bars represent the volume frequency (\%) of the particles, whereas red line represents the cumulative volume (\%) of the particles.

### 4.3.2 Emission Spectroscopy

Emission spectroscopy is an useful accepted optical technique for plasma diagnostic. This technique is considered as non-perturbing method and is based on the analysis of the light emitted by the plasma.

Due the collisional excitation of the chemical species present in the plasma core is quite strong, the corresponding quantum levels population becomes high enough for net emission from the plasma (Boulos et al. 1986).

Assuming that plasma is in the state of local thermodynamic equilibrium (LTE), it is likely to deduce plasma parameters such as species densities and temperature from spectroscopic observations.

Because the low energy involved in the rotation process, the rotational temperature can be assumed as the kinetic temperature of the gas as proposed by Mermet 1978, Reeve and Weimer 1995, and Lange et al. 1999. Hence, measurements of relative intensities of rotational lines reflect the overall gas temperature.

The emission spectrum was recorded in the 516 nm spectral band, which corresponds to the Swan band system (see transition scheme 4.1) emitted by the \(C_2\) radicals.
\[ a^3 \prod_{\nu=1}^{n} \nu = 0 \implies a^3 \prod_{\nu}^n \nu^n = 0 \]  

(4.1)

As reviewed in Chapter 2, it is generally accepted that C_2 radicals play an important role in the fullerene formation under plasma conditions. In this study the Swan band emitted by the C_2 radicals was used to determine their overall temperature and column densities at different operating conditions.

The temperature and C_2 species concentration determination was performed using relative line intensities. Two spectroscopic methods were used for the measurement computations: the self-absorption and the Boltzmann plot methods.

In the self-absorption method (Lange et al. 1999), the intensity of a rotational line emitted by a plasma column of length \( L \) can be related with the respective average emission coefficient by (Lange et al. 1999):

\[ I_{J'J} = \int \frac{\epsilon_{J'J}(\nu) L}{\kappa(\nu)L}(1 - e^{-\kappa(\nu)L}) \, d\nu \]  

(4.2)

Where \( \epsilon_{J'J}(\nu) \) and \( \kappa(\nu) \) are the spectral line emission and absorption coefficients respectively.

The spectral absorption coefficients include contributions from all the possible rotational transitions between both electronic states.

Additionally, the emission and absorption coefficients of the rotational lines depend on the column density and temperature according to:

\[ \epsilon_{J'J'}(\nu) = \frac{2 \pi \hbar c^2}{m} \frac{\nu_{J'J'}}{\nu} f_{mn} q_{\nu_{J'} \nu} S_{J'J} \exp \left( \frac{E_n + E_J}{kT} \right) Q_{J'J}^{-1} N_{\nu} L \]  

(4.3)

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\[ \kappa_{J',J} L = \frac{\pi e^2}{mc^2} S_{J',J} f_{mn} q_{v'v''} \exp \left( \frac{E_{J''}}{kT} \right) Q_{v''}^{-1} N_{m,v'} L \] (4.4)

Where \( N_{m,v'} L \) is the column density of \( C_2 \) (a \( ^3\Pi_u, v''=0 \)), \( f_{mn} \) is the electronic oscillator strength, \( q_{v'v''} \) is the Frank-Condon factor, \( v \) is the mean wave number, \( E_{J'} \) and \( E_{J''} \) are the rotational levels in the upper and ground states, \( S_{J',J} \) is the Hönzl-London factor, \( J'(J'') \) is the rotational quantum number of the total angular momentum, and \( Q_{v'} \) and \( Q_{v''} \) are the rotational statistical sums for \( d \ ^3\Pi_g \) and \( \Pi_u \) states respectively.

The method is based on the fact that the intensity of the \( P(0,0) \) band head is more decreased than the intensity of the resolved rotational components. This intensity decreasing of the band head is due to the self-absorption effect. Thus, the method uses the integrated intensity of the normalized band intensity (normalized \( (0,0) \) band) as a measure of the \( C_2 \) density. The intensity of the normalized band is an increasing function of the column density.

Direct fitting of measured to calculated spectra was used to perform the simultaneous estimation of the temperature and \( C_2^+ \) density. A set of normalized intensity distributions was calculated. The temperature ranged from 2750 to 8375 K with an increment of 125 K. The column density ranged from \( 10^{12} \) to \( 10^{16} \) cm\(^{-2} \) with an increment of \( 5 \times 10^{14} \) cm\(^{-2} \) for each temperature.

After recording of the experimental spectra, the temperature and column density can be calculated as the parameters that minimize the expression:

\[ A(T, NL) = \sum_{i=1}^{n} \left[ I_{\text{exp}}^i - I_{\text{calc}}^i (T, NL) \right]^2 \] (4.5)

Where \( I_{\text{exp}}^i \) and \( I_{\text{calc}}^i (T, NL) \) are the characteristic peaks in the rotational structure for the experimental and simulated spectra respectively, and \( n \) is the number of \( P+R \) lines under analysis.
On the other hand, if a rotational temperature is known the column density can be related to the experimental value of the normalized band intensity.

Thus in the second method, the temperature was estimated using the Boltzmann plot procedure. This temperature was obtained taking into consideration 12 quite good resolved rotational components of the P(0-0) branch.

Similarly to the determination of the excited temperature, the rotational temperature of a molecule can be estimated using the rotational line intensity (Mermet 1978). For a $J' - J''$ transition, this intensity can be calculated by (Mermet 1987):

$$I = Dv^4 S \exp\left(-\frac{E_r}{kT_r}\right)$$  \hspace{1cm} (4.6)

Where $D$ contains the rotational partition function, the statistical weight $(2J' + l)$ and universal constants, and $S$ the oscillator strength and $E_r$ is the rotational energy of the upper level of the line.

The final equation can be expressed as:

$$\ln\left(\frac{I}{S}\right) = Dv^4 - \frac{E_r}{kT_r}$$  \hspace{1cm} (4.7)

Where

$$S = \frac{[(J'+1)^2 - 1]}{(J'+1)}$$  \hspace{1cm} (4.8)
\[ E_r = B \nu J' (J'+1) \] (4.9)

Where \( J' \) is the rotational quantum number of the upper rotational state = \( J''+J \) for the P branch, \( B \nu \) is the rotational constant for the upper vibrational state and \( \nu \) is the wave number of the line.

Thus, the temperature \( T_r \) can be deduced from the slope of plotting \( \ln( I / S ) \) versus \( E_r \) from equation 4.7.

A typical experimental spectrum of \( \text{C}_2 \) radicals is shown in Figure 4.5, along with (+) markers resulting from the simulated spectrum fitting. In this figure, it can be also seen two high peaks related to the nickel atomic lines.

Figure 4.5 Experimental Spectrum of \( \text{C}_2 \) Radicals and (+) markers of the Simulated Fitting for a Temperature of 5000 K
The light emitted by the plasma jet was projected onto the spectrometer entrance slit through a quartz window using double achromatic lens with 3-cm focal point. A typical silica fused optical fiber was used to collect the light emitted by the plasma. The lens is placed parallel to the window 10 cm from the plasma center and 8 cm from the plasma torch exit (see Figure 4.6). The emission signal was selected by a 1-m monochromator (JY/HR-1000) supplied with a grating of 1200 grooves/mm. The linear dispersion of the monochromator grating operating in the first order is 7.8 Å/mm. The output spectrum is connected either to a photomultiplier Hamamatsu (model R928) or to OMA having 1024 x 256 photodiode matrix (from Princeton Instrument, Inc.).

![Diagram of Optical Set-Up]

Figure 4.6 Schematic of Optical Set-Up

In this condition, the spectrum was obtained without spatial distribution and only an average of the light intensity emitted by the plasma tail flame was measured and processed. These measurements allowed estimating overall temperatures and C2 species concentrations on the tail flame.
In this way, the estimated temperatures and \( C_2 \) concentrations can be only considered as overall properties of the vaporization process that depend of the operating parameters. In other words, temperature and \( C_2 \) concentration estimated in this work do not represent plasma properties. Temperature and \( C_2 \) concentration were evaluated using the overall light intensity emitted by the whole plasma tail. By comparing these overall properties between the experimental tests, it is possible to study the effect of operating parameters on the fullerene synthesis. Additionally, these comparisons may be correlated with the theoretical results obtained in the thermodynamic and kinetic studies.

At this point, it is important to remark that all the estimations of temperatures and \( C_2 \) concentrations were computed by Prof. Hubert Lange from the Department of Chemistry from Warsaw University.

4.3.3 Ultraviolet (UV) Absorption Spectrophotometry

UV spectroscopy represents a powerful analytical tool for characterizing fullerene molecules. This technique is based on the fact that fullerenes exhibit size- and structure-dependent UV absorption spectra. These spectra are due to the electronic transitions within the clusters.

Qualitatively, pure \( C_{60} \) solutions show a deep purple color whereas \( C_{70} \) solutions exhibit a wine red color. A representative spectrum for \( C_{60} \) fullerene is shown in Figure 4.7. \( C_{60} \) fullerene exhibits a characteristic absorption pick at 329 nm.

This technique was used to qualitatively analyze \( C_{60} \) fullerene yield produced in the experimental tests. The UV absorption spectrometer was a Biochrom Ultrospec 2100-Pro operating in a 190 – 900 nm wavelength range. The instrument was calibrated using \( C_{60} \) fullerene standard 95.5 \% purity from Hoechst AG Company. The standard samples were prepared by dissolving specific quantities of \( C_{60} \) fullerene into 200-ml of toluene and analyzed at 329-nm wavelength. The calibration curve is shown in the Figure 4.8. The regression coefficient and the standard error were estimated as 0.9991 and 0.00016, respectively.
Figure 4.7  UV-Visible Absorption Spectra of a Purified Sample of C₆₀ Dissolved in Toluene Solvent for the Test CB09

Figure 4.8  Calibration Curve of the UV-VIS Spectrophotometer using a C₆₀ Standard of 95.5% Purity
The sample preparation procedure involved the following steps. In the first step, 0.2 g of soot was dispersed in 100-ml of toluene in a sonication bath for 15 min. Then, the solution was filtered using a # 40 filter paper. The resulting filtrate, a red-brown solution containing the dissolved fullerene molecules, was analyzed by the UV spectrometer.

4.3.4 High Performance Liquid Chromatography (HPLC)

Chromatography is an analytical method that has been widely used for the separation, identification and determination of fullerenes. Theses fullerenes are usually part of a complex mixture of carbon structures. In general, chromatography is a technique in which a mixture of components is separated based on the rates at which they are carried through a stationary phase by a gaseous or liquid mobile phase. High performance liquid chromatography (HPLC), so named because the mobile phase is a liquid, has been the main chromatographic technique used to determine the fullerene concentrations.

The basic components of a typical liquid chromatograph are the following: 1) a pump to force the mobile phase through the system, 2) sampling valves and loops to inject the sample into the mobile phase, 3) a separation column, 4) a detector, and 5) a readout device. The Figure 4.9 shows a schematic diagram of a high performance liquid chromatograph.

Ultraviolet (UV) detectors have been widely used in the fullerene determination. The detector operation principle is based on the ultraviolet radiation absorbed by a sample. A readout device monitors the absorbed radiation to estimate the concentration of the component.

Because the fullerene molecules contain strong UV-absorbing groups, their detection is usually easy to perform. The HPLC-UV method for the determination of fullerenes in soot extractions achieved excellent results.

Table 4.3 summarizes the main operating parameters of a successful method using HPLC-UV detection to determine the fullerene concentration of a soot extraction. The chromatographic method is performed using a sample of the fullerene extraction, which is obtained according to the fullerene extraction procedure described in the paragraph 4.3.3.
Figure 4.9  Schematic of a High Performance Liquid Chromatograph Equipment

TABLE 4.3  HPLC METHOD TO ANALYZE FULLERENE MOLECULES

<table>
<thead>
<tr>
<th>Component</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Valve</td>
<td>10-μl-sample loop.</td>
</tr>
<tr>
<td>Column</td>
<td>Cosmosil Buckyprep 4.6 x 250 mm</td>
</tr>
<tr>
<td>Detector</td>
<td>UV Detector.</td>
</tr>
<tr>
<td></td>
<td>Wavelength: 340 nm</td>
</tr>
<tr>
<td>Elution</td>
<td>Mobile phase: toluene</td>
</tr>
<tr>
<td></td>
<td>Flow rate: 1 ml/min</td>
</tr>
<tr>
<td></td>
<td>Sample volume: 10 μL</td>
</tr>
</tbody>
</table>

The chromatographic method was developed in the Laboratory of Plasma Chemistry of the Department of Chemistry at Warsaw University in Poland. All the HPLC analyses were also performed in this laboratory thanks to the help of Prof. Andrzej Huczko.
The instrument was calibrated using a mixture of \( C_{60}, C_{70}, C_{78} \) and \( C_{84} \) fullerene standards. The Figure 4.10 depicts a typical chromatogram obtained from the analysis of the fullerene standards mixture.

![Figure 4.10 HPLC Chromatogram of a Mixture of Fullerene Standards Dissolved in Toluene](image)

The specific retention time for each fullerene molecule was determined as shown in Table 4.4.

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{60} )</td>
<td>7.30</td>
</tr>
<tr>
<td>( C_{70} )</td>
<td>12.57</td>
</tr>
<tr>
<td>( C_{78} )</td>
<td>19.70</td>
</tr>
<tr>
<td>( C_{84} )</td>
<td>24.50</td>
</tr>
</tbody>
</table>
As expected, the retention time of fullerenes depends on the number of carbon atoms, the shape and the structural configuration of the molecule.

### 4.3.5 Surface Area

Surface area is an important property used to classify carbon black powders. For example, for non-porous carbon black, the surface area values are inversely correlated with the particle size.

Surface area analyses were carried out trying to evaluate the effectiveness of the synthesis of fullerenes and nanotubes during the experimental part. A significant increase in the soot surface area with respect to the original starting material surface area will be related with a structural change on the carbon particles. As a consequence, the formation of fullerenes is expected.

The surface area analyses were performed following the typical standard tests method used for the evaluation of carbon black powders (ASTM D 5816 – 96).

The surface area of the powders was measured according to the method of Brunauer, Emmet and Teller (BET) using an analyzer of type QUANTACHROME Autosorb 1. A multipoint plot was used to carry out the measurements and nitrogen was used as adsorbate. BET error was estimated about +/- 2 m²/g.

### 4.3.6 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measures the changes in mass of a sample when it is subjected to a controlled temperature program. The temperature program is most often a linear temperature increase, however isothermal studies can also be carried out if the changes in sample mass with time are recorded.
Because TGA is inherently quantitative, it is an extremely powerful thermal technique to quantify the concentration of the different carbon structures produced in the fullerene synthesis process as reported by Rinzler et al. (1998) and Shi et al. (2000).

TGA were performed using a SETERAM SETSYS 24 TG analyzer. The essential instrument components are a recording balance, a furnace, a temperature programmer, a sample holder, an enclosure for establishing the required atmosphere, and a means of data recording and displaying.

The results usually show the plot of the TGA, the heat flux and the differential thermogravimetric (DTG) curves. The DTG curve is often useful in revealing extra details such as inflection points on the TG curve. These points provide references for weight change measurements in systems where the weight losses are not completely resolved.

![Graph showing TG analysis](image)

**Figure 4.11**  TG Analysis of a Purified C₆₀ Sample form Test CB08
TG and DTG curves are used in fullerene and nanotube characterization to selectively analyze the different CNSs, taking into account their specific combustion behavior.

The TGA procedure (Shi et al., 2000) involved a soot sample of 15 mg, a temperature program from room temperature to 900 °C with a ramp rate of 10 °C/min and an oxidizing atmosphere with air flow rate of 70 cm³/s.

Figure 4.11 depicts the TG and heat flux curves of a C₆₀ sample. In this figure, dₘ represents the weight percent related to the oxidation reactions for each carbon structure. The sample was extracted according to the extraction procedure described in the paragraph 4.3.3. The solvent was freely evaporated at room temperature.

4.3.7 Scanning Electron Microscopy (SEM)

Typical external diameters of carbon nanoparticles fall in the range of 1 to 100 nm. Carbon nanotube lengths can reach up until 250 μm. At these scales, SEM is well suited for analysis of the carbon nanostructures. A LEO 1530 Field Emission Scanning Electron Microscope was used to characterize the morphology of carbon nanostructures produced in the plasma process.

The operating parameters used during the analysis were an acceleration tension of 1 kV and a work distance of 8.5 mm.

The sample was prepared by dispersing several milligram of soot on a sample brass bearing with a double side sticker using an argon jet at a pressure of 2.7 kPa (40 psig). A dispersion distance of 10 cm was used during the powder dispersion.

Under these conditions, it was possible to analyze the nanometric details of the carbon nanostructures and magnifications on the order of 200,000 X were reached.

4.3.8 Transmission Electron Microscopy (TEM)

Although scanning electron microscopy can reveal important external features of the carbon nanoparticles, TEM techniques allows, in a first approximation, to determine their internal
structure. TEM is one of the most powerful microscopic techniques to carbon nanostructure characterization because of the ultra high magnifications reached. For instance, using TEM is possible to better characterize morphologically and structurally carbon nanostructures. TEM magnifications are on the order of 450,000 X.

A Hitachi H-750 Transmission Electron Microscope was used with an acceleration tension of 125 kV and an electron microscope film 4489.

For the sample preparation, several milligrams of soot were dispersed in ethylic alcohol using a sonication bath for 1 min. A 20-μl sample of the dispersed solution was placed on a copper support and analyzed.
CHAPTER 5  TEMPERATURE AND VELOCITY PROFILES OF THE RF
PLASMA TORCH AND VAPORIZATION STUDY OF CARBON
PARTICLES.

Mathematical modeling is an excellent tool that has been widely used to calculate the
temperature, flow and concentration fields in induction plasma torches (Proulx et al., 1985,
Watanabe et al., 1990, Cai et al., 1995, Nishiyama et al., 1996, Xue et al., 2001). In general, a
complete mathematical model for fullerene formation should include mathematical
formulations for two-temperature helium ICP (Cai et al., 1995), for particle vaporization and
for kinetic formation of fullerene. Although the results of this model would provide a great
deal of insight on the temperature and flow patterns within the plasma and reactor, the
developing of the complete mathematical model for describing fullerene formation represent a
major undertaking and is well beyond of the scope of the present study.

5.1  Plasma Temperature and Velocity Profiles

The computational code developed by Siwen Xue (CRTP, Université de Sherbrooke) was
used to evaluate the dynamic behavior of the RF plasma torch.

The assumptions and conservation equations used in the mathematical model were formulated
by Siwen and can be found in Xue et al., 2001.

Because this model was not developed in the frame of this work, only the computational
results obtained are presented. These results allowed estimating average plasma properties
such as temperature and residence time. These average plasma properties were used to
evaluate the particle temperature and vaporization time in a subsequent vaporization study.

At this point, it is important to remark that the mathematical model only involves the
prediction of the flow and temperature field in the plasma and does not involve the prediction
of the particle trajectory and its temperature history. In other words, the vaporization model was non-coupled with that used in the plasma simulation.

It is clear that the results of a vaporization study using average plasma properties do not constitute conclusive proof on the dynamic of the vaporization process. However, for the purpose of this discussion, these results may be deemed satisfactory.

The plasma mathematical model was solved for a Tekna PL-50 torch geometry with a 50-mm id plasma confinement tube. Details of the principal dimensions of the torch are depicted in Figure 5.1. Temperature, flow and velocity profiles were simulated for two different conditions of plasma gas: pure argon and argon-helium mixture. Table 5.1 shows the torch characteristic dimensions and operating conditions used in both simulations.

Figure 5.1  Principal Dimensions of the RF Induction Plasma Torch
TABLE 5.1  TORCH CHARACTERISTIC DIMENSIONS AND OPERATING CONDITIONS

<table>
<thead>
<tr>
<th>Torch Dimensions</th>
<th>Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_0$ 30 kW</td>
<td>Argon Plasma</td>
</tr>
<tr>
<td>$f$ 3 MHz</td>
<td>$Q_1$ 5 slpm</td>
</tr>
<tr>
<td>$L_0$ 50 mm</td>
<td>$Q_2$ 35 slpm (Ar)</td>
</tr>
<tr>
<td>$L_1$ 60 mm</td>
<td>$Q_3$ 120 slpm (He)</td>
</tr>
<tr>
<td>$L_T$ 250 mm</td>
<td>Argon-Helium Plasma</td>
</tr>
<tr>
<td>$r_1$ 3.7 mm</td>
<td>$Q_1'$ 5 slpm (Ar)</td>
</tr>
<tr>
<td>$r_2$ 18.8 mm</td>
<td>$Q_2'$ 35 slpm (Ar)</td>
</tr>
<tr>
<td>$R_0$ 25 mm</td>
<td>$Q_3'$ 120 slpm (He)</td>
</tr>
<tr>
<td>$R_c$ 33 mm</td>
<td></td>
</tr>
</tbody>
</table>

5.1.1  Argon Plasma

Figure 5.2 shows the temperature, streamline and velocity profiles for argon plasma. A recirculating eddy is formed in the top of the plasma because of a strong inward radial flow induced by the electromagnetic pumping in the coil region. Isotherms show that the highest temperature (11,500 K) exists in the coil region and is off-center. A laminar flow is also observed downstream from the high temperature region.

According to Figure 5.2, the axial velocity in the central region of the plasma increases initially and then decreases steeply to the wall. The isocontours of the axial velocity show that the highest velocity (56 m/s) is located close the center of the plasma. Because the axial injection of carbon powder, it is expected that plasma-particle interactions take place mainly in the centerline of the plasma. The temperature and velocity distributions along the mainstream are shown in Figure 5.3. The highest temperature (~9000 K) and velocity (~56 m/s) are reached about 0.10 m downstream from the injection point.
Figure 5.2  Temperature, Stream Function and Axial Velocity Isocontours for a RF Induction Plasma Torch. Po = 30 kW, P = 66 kPa, Q₁ = 5 slpm Ar, Q₂ = 35 slpm Ar and Q₃ = 120 slpm Ar.

Figure 5.3  Plasma Temperature and Velocity at the Mainstream of the RF Plasma Torch. Po = 30 kW, P = 66 kPa, Q₁ = 5 slpm Ar, Q₂ = 35 slpm Ar and Q₃ = 120 slpm Ar.
5.1.2 Argon-Helium Plasma

A similar recirculating eddy is observed in argon-helium plasma (Figure 5.4). Streamlines show that the recirculating eddy is stronger than that found in argon plasma. This effect might be induced by strong Lorentz force attributed to the helium addition. It is expected that strong eddy results in uniform distribution of reactant species downstream from the high temperature zone. As expected, argon-helium plasma results in lower temperatures as compared with argon plasma.

Figure 5.4 Temperature, Stream Function and Axial Velocity Isocontours for a RF Induction Plasma Torch. $P_0 = 30$ kW, $P = 66$ kPa, $Q_1 = 5$ slpm Ar, $Q_2 = 35$ slpm Ar and $Q_3 = 120$ slpm He
Such as argon plasma, the isotherms show that the highest temperature (11600 K) is located in the center of the plasma coil. The temperature gradient is gentler near the ceramic confinement. When helium is fed as sheath gas, a cooling effect is presented in the plasma tail due to the higher thermal conductivity of helium (0.2256 W/m K at 500 K) than argon (0.0267 W/m K at 500 K). In both plasmas, the highest plasma temperatures are found in the central region from $r = 0$ to $r = 0.010$ m. Because the particle-feeding probe is placed in the center of the plasma torch, it is expected that carbon particles be exposed to the highest plasma temperatures. Although argon-helium plasma presents lower temperatures along the plasma tail than argon, higher vaporization rates of carbon particles are observed, as it will be shown later in this Chapter. The higher thermal conductivity of helium also enhances the vaporization rate of the particle.

The axial velocity in the central and intermediate region decreases with helium injection. Because the low density of helium, the incoming flow has low momentum. Helium addition causes a strong eddy and modifies the velocity fields. The highest axial velocities are closer to the ceramic tube as compared with argon plasma. The temperature and velocity distributions along the axis are shown in Figure 5.5.

---

**Figure 5.5**  Plasma Temperature and Velocity at the Mainstream of the RF Plasma Torch. $P_o = 30$ kW, $P = 66$ kPa, $Q_1 = 5$ slpm Ar, $Q_2 = 35$ slpm Ar and $Q_3 = 120$ slpm He.
The temperature attains a maximum value of about 9000 K 0.07 m downstream from the injection point of the powder. Highest velocity of about 58 m/s is reached at 0.13 m from the injection point. Taking into account the high thermal conductivity of helium, it was estimated (see 5.2) that these plasma conditions favour carbon particle vaporization and carbon-carbon reactions during the synthesis of fullerenes, as compared with argon plasma. Argon-helium plasma with high thermal conductivity at high temperature (9000 K) and velocity (58 m/s) might better vaporize carbon particles than argon plasma at the same conditions. Similar residence time of the particles are expected in both argon and argon-helium plasmas due to their axial velocities (argon, 56 m/s and argon-helium, 58 m/s). However, at high temperature (9000 K), argon-helium plasma presents higher heat transfer than argon plasma. The higher heat transfer of argon-helium plasma enhances particle vaporization and increases carbon vapor pressure inside the reactor. According to the thermodynamic and kinetic studies (Chapter 3), a high gas carbon concentration is considered to play a key role in the fullerene synthesis. Furthermore, high temperatures also favour fullerene formation via the sequential additions of both C₂ and C₃ precursors.

It should be noted that the validity of these assumptions is limited since the models do not take into account any particle sublimation phenomena.

The effects of the carbon particles feed rate and operating pressure were not theoretically studied. However, as the carbon particle feed rate is increased, the temperature of the plasma tail is expected to be decreased due to the endothermic energy requirements to sublime carbon particles ($\Delta H_v = 396$ kJ/mol) and heat their gaseous products.

At lower operating pressure (44 kPa), it is expected that the plasma tail be extended due to the higher expansion rates of the plasma gas. Therefore, as the operating pressure is decreased, temperature isocontours are expected to increase. Higher expansion rates also involve a higher plasma velocities and smaller residence times of the particles in the hot zones of the plasma. Thus, a low operating pressure might enhance zones of high temperature in the plasma but at the same time, reduce the residence time of the particles inhibiting their complete vaporization.
5.2 Particle Vaporization Study

Since particle vaporization process strongly influences carbon vapor pressure inside the plasma reactor, a particle vaporization study was performed in the zone of high temperature of the plasma torch. Poor particle vaporization is considered to be responsible of a low fullerene yield.

Speculating that carbon particles travel to the same velocity of the plasma gas, the residence time of the particle in the plasma tail was estimated using the computational results obtained above. The residence time was computed in the centerline (r = 0) and from 0.110 to 0.250 m downstream of the plasma tail zone. Figures 5.3 and 5.5 show plots of temperature and axial velocity of the mainstream (r = 0) as a function of the axial direction. The temperature range was from 450 to 9100 K for argon plasma and from 570 to 9180 K for helium plasma. The residence time ($t_r$) of the mainstream between two isotherms, $T_1$ and $T_2$, was approximated according to the equation:

$$t_r = \frac{Z_2 - Z_1}{V}$$  (5.1)

Where $Z_1$ and $Z_2$ are the axial distance of two consecutive points and $V$ is the average velocity between the two points.

The total residence time was estimated as the sum of the residence times measured incrementally over the whole distance.

The residence time for argon plasma at 30-kW plate power and 66 kPa was estimated to be about 3.3 ms, whereas for argon-helium plasma the estimated residence time was 3.2 ms.

Particle vaporization calculations were carried out according to the shrinking kinetic model and taking into account a residence time for the particles about 3.3 ms.
In this case, the vaporization rate of a carbon black particle can be represented as a first-order reaction

\[
\frac{dm_p}{dt} = -km_p
\]  

(5.2)

Where \( m_p \) is the mass of the carbon particle, \( t \) is the time and \( k \) is the constant of vaporization rate.

For spherical particle with constant density, the vaporization rate becomes

\[
\frac{dd_p}{dt} = -\frac{k}{3} d_p
\]  

(5.3)

Where \( d_p \) is the diameter of the particle.

Integrating from \( d_p = d_o \) to \( d_p = d_p \) for \( t = 0 \) to \( t = t \)

\[
\ln \left( \frac{d_p}{d_o} \right) = -\frac{k}{3} t
\]  

(5.4)

If \( \tau \) is the time for the complete particle vaporization \((d_p \sim 1 \times 10^{-10 }\text{ m})\), then
\[
\tau = \frac{3 \ln \left( \frac{1 \times 10^{-10}}{d_o} \right)}{k}
\]  
(5.5)

Taking into account the residence time of the particle into the plasma flame (3.3 ms), the vaporized fraction of the particle \( f_v \) might be estimated by the equation:

\[
f_v = 1 - \exp \left( -\frac{k}{3} t_r \right)
\]  
(5.6)

Where \( t_r \) is the residence time of the particle and \( k \) is the constant of vaporization rate expressed as an Arrhenius equation

\[
k = A_0 \exp \left( -\frac{E}{RT_p} \right)
\]  
(5.7)

Where \( A_0 \) is the pre-exponential factor, \( E \) is the activation energy, \( R \) is the gas constant and \( T_p \) is the particle temperature.

The particle temperature can be determined by a steady-state energy balance (Vardelle et al., 1983, Proulx et al., 1985, Borman and Ragland, 1998).

\[
Q = A_p \rho c (T - T_p) - \sigma A_p (T_p^4 - T_a^4)
\]  
(5.8)
Where $Q$ is the heat exchange between the particle and its surroundings, $A_p$ is the particle surface area, $h_e$ is the heat transfer coefficient, $\sigma_s$ is the Stefan–Boltzmann constant, $\varepsilon$ is particle emissivity and $T$, $T_p$, and $T_a$ is the temperature of the plasma, particle and surroundings, respectively.

The first term on the right hand side of the equation 5.8 represents the conductive and the convective heat transfer between the particle and the plasma. The second term represents the heat transfer by radiation from the particle surface to the surroundings.

Considering direct particle sublimation, the net heat exchange between the particle and the surroundings is expressed by,

$$Q = -\frac{dm_p}{dt} \Delta H_s$$  \hspace{1cm} (5.9)$$

Where $\Delta H_s$ is the latent heat of sublimation of carbon particles.

Equation 5.9 for a spherical particle becomes

$$Q = -\frac{1}{2}\pi \rho_p d_p^2 \Delta H_s \frac{d \rho_p}{dt}$$  \hspace{1cm} (5.10)$$

Where $\rho_p$ is the particle density.

In this case the particle temperature is assumed to be uniform due to the thermal conductivity of the particle material ($k_p$) is much higher than the gas ($k^{-}$).
\[ Bi = \frac{\bar{k}}{k_p} \ll 0.01 \quad (5.11) \]

Combining equations 5.8 and 5.10 and integrating from \( d_p = d_o \) to \( d_p = 0 \) for \( t = 0 \) to \( t = \tau \),

\[ h_c (T - T_p) - \sigma \epsilon (T_p^4 - T_a^4) - \frac{d_o \rho_p \Delta H_s}{2\tau} = 0 \quad (5.12) \]

Combining equation 5.5 and 5.12, the final expression for calculating the particle temperature becomes.

\[ h_c (T - T_p) - \sigma \epsilon (T_p^4 - T_a^4) - \frac{d_o \rho_p \Delta H_s A_o \exp \left( -\frac{E}{RT_p} \right)}{6 \ln \left( \frac{1 \times 10^{-10}}{d_o} \right)} = 0 \quad (5.13) \]

Where \( h_c \) was calculated using a Nusselt number of 2.0 according to the equation 5.14. Here, it was supposed that particle moves through the fluid at the same velocity than plasma gas.

\[ Nu = \frac{h_c d_p}{\bar{k}} \quad (5.14) \]
In this study, the droplet size analyzer described in Chapter 4 was used to determine the mean diameter and the particle size distribution of the carbon black-nickel mixture. Three different tests were carried out using a 4 %mol catalyst-ratio mixture. The mean particle diameter and the associated span are shown in Table 5.2.

TABLE 5.2 PARTICLE SIZE OF THE CARBON BLACK-NICKEL MIXTURE

<table>
<thead>
<tr>
<th>Run</th>
<th>Mixture Flow Rate (g/min)</th>
<th>Gas Flow Rate (slpm)</th>
<th>Mean Particle Diameter (μm)</th>
<th>Span</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>8</td>
<td>144</td>
<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>8</td>
<td>96</td>
<td>1.62</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>8</td>
<td>101</td>
<td>1.53</td>
</tr>
</tbody>
</table>

$X^* = 115 \quad S_x = 57$

Additionally, Table 5.3 shows the thermodynamic, kinetic and physical properties used in the calculations.

The average plasma temperature for argon plasma in the mainstream was estimated to be about 7000 K, while for argon-helium plasma was 8000 K.

Thus, 7500 K was used as average plasma temperature for the experiments at 40 kW of plate power and 5000 K for the experiments at 20 kW.

Using these plasma temperatures and the average particle size shown in Table 5.2, the particle temperature, the time for a complete particle vaporization and the vaporized fraction of the particle were calculated. The results for argon and argon-helium plasmas are shown in Table 5.4.

Taking into account the estimated residence time of 3.3 ms, it might be concluded that a poor vaporization process is observed in argon plasma. When the average plasma temperature is about 7500 K, only particles smaller than 50 μm can be completely vaporized, while larger particles present higher vaporization times.
The vaporized fraction of various particle sizes (50 – 200 μm) ranged from 0.27 to 0.92 at low plasma temperature (5000 K) and from 0.67 to 1.00 at high plasma temperature (7500 K).

**TABLE 5.3** THERMODYNAMIC AND PHYSICAL PROPERTIES USED IN THE PARTICLE VAPORIZATION COMPUTATIONS

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon Forming Gas Enthalpy, $H_g$, kJ/kg</td>
<td>0.0</td>
<td>1</td>
</tr>
<tr>
<td>Helium Forming Gas Enthalpy, $H_g$, kJ/kg</td>
<td>3085.00</td>
<td>1</td>
</tr>
<tr>
<td>Water Specific Heat, $C_p$, kJ/kg K</td>
<td>4.18</td>
<td>2</td>
</tr>
<tr>
<td>Solid Carbon Enthalpy, $h_{C_0}$, kJ/kg</td>
<td>-4.45</td>
<td>3</td>
</tr>
<tr>
<td>Gas Carbon Enthalpy, $H_{C_0}$, kJ/kg</td>
<td>7.00 X 10^4</td>
<td>3</td>
</tr>
<tr>
<td>Pre-Exponential Factor, $A_p$, s^-1</td>
<td>3.7 X 10^5</td>
<td>4</td>
</tr>
<tr>
<td>Activation Energy, $E$, J/mol</td>
<td>7.30 X 10^4</td>
<td>4</td>
</tr>
<tr>
<td>Gas Constant, $R$, J/mol K</td>
<td>8.3</td>
<td>2</td>
</tr>
<tr>
<td>Stefan-Boltzmann Constant, $\sigma_n$, J/m²s K^4</td>
<td>5.67 X 10^-8</td>
<td>6</td>
</tr>
<tr>
<td>Carbon Particle Emmissivity, $\varepsilon$</td>
<td>0.8</td>
<td>2</td>
</tr>
<tr>
<td>Carbon Latent Heat of Vaporization, $H_l$, J/kg</td>
<td>3.3 X 10^7</td>
<td>5</td>
</tr>
<tr>
<td>Carbon Thermal Conductivity, $K_p$, J/m s K</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>Carbon Particle Density, $\rho_p$, kg/m³</td>
<td>2200</td>
<td>3</td>
</tr>
</tbody>
</table>

References
1 Boulos et al. (1994)
2 Weast and Lide, (1990)
3 FactSage, (2001)
4 Smith and Smoot, (1980)
5 Goldsmith et al., (1961)
6 Borman and Ragland, (1998)

In contrast, argon-helium plasma presents a higher particle heat transfer and the vaporization time is reduced, at same plasma temperatures than argon. For example, at low plasma temperature (5000 K), 50-μm particles can be completely vaporized, whereas at high temperatures (7500 K) even 100-μm particles are completely vaporized. Furthermore, argon-helium plasma at high plasma temperatures is able to vaporize until 89% of large carbon particles (200 μm). In fact, for particle sizes from 50 to 200 μm, the vaporized fraction of carbon particles ranged from 0.54 to 1.00 at low plasma temperature (5000 K). At high plasma temperature, the vaporized fraction of particles was from 0.89 to 1.00.
From the results, it is clear that argon-helium plasma enhances particle vaporization, and as consequence, carbon vapor is increased inside the plasma reactor.

According to kinetic study, high concentrations of carbon gas species favour fullerene formation, thus it is expected that fullerenes be produced in the reactor zone.

<table>
<thead>
<tr>
<th>Plasma Temperature (K)</th>
<th>Particle Diameter (m)</th>
<th>Particle Temperature (K)</th>
<th>Evaporation Time (ms)</th>
<th>Vaporized Fraction (f_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon Plasma</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>5.0 X 10^{-5}</td>
<td>1730</td>
<td>23.0</td>
<td>0.92</td>
</tr>
<tr>
<td>5000</td>
<td>1.0 X 10^{-4}</td>
<td>1420</td>
<td>72.0</td>
<td>0.57</td>
</tr>
<tr>
<td>5000</td>
<td>1.5 X 10^{-4}</td>
<td>1300</td>
<td>132.0</td>
<td>0.37</td>
</tr>
<tr>
<td>5000</td>
<td>2.0 X 10^{-4}</td>
<td>1230</td>
<td>199.0</td>
<td>0.27</td>
</tr>
<tr>
<td>7500</td>
<td>5.0 X 10^{-5}</td>
<td>2060</td>
<td>10.0</td>
<td>1.00</td>
</tr>
<tr>
<td>7500</td>
<td>1.0 X 10^{-4}</td>
<td>1720</td>
<td>25.0</td>
<td>0.92</td>
</tr>
<tr>
<td>7500</td>
<td>1.5 X 10^{-4}</td>
<td>1570</td>
<td>41.0</td>
<td>0.78</td>
</tr>
<tr>
<td>7500</td>
<td>2.0 X 10^{-4}</td>
<td>1490</td>
<td>56.0</td>
<td>0.67</td>
</tr>
<tr>
<td>Argon-Helium Plasma</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>5.0 X 10^{-5}</td>
<td>2340</td>
<td>6.0</td>
<td>1.00</td>
</tr>
<tr>
<td>5000</td>
<td>1.0 X 10^{-4}</td>
<td>1750</td>
<td>23.0</td>
<td>0.93</td>
</tr>
<tr>
<td>5000</td>
<td>1.5 X 10^{-4}</td>
<td>1530</td>
<td>48.0</td>
<td>0.72</td>
</tr>
<tr>
<td>5000</td>
<td>2.0 X 10^{-4}</td>
<td>1410</td>
<td>80.0</td>
<td>0.54</td>
</tr>
<tr>
<td>7500</td>
<td>5.0 X 10^{-5}</td>
<td>3030</td>
<td>3.0</td>
<td>1.00</td>
</tr>
<tr>
<td>7500</td>
<td>1.0 X 10^{-4}</td>
<td>2140</td>
<td>9.0</td>
<td>1.00</td>
</tr>
<tr>
<td>7500</td>
<td>1.5 X 10^{-4}</td>
<td>1850</td>
<td>18.0</td>
<td>0.97</td>
</tr>
<tr>
<td>7500</td>
<td>2.0 X 10^{-4}</td>
<td>1690</td>
<td>28.0</td>
<td>0.89</td>
</tr>
</tbody>
</table>

If the plasma average temperature is about 7500 K, it is also expected to find a temperature range form 2250 to 3800 K in the reactor zone as shown in 5.3. From the thermodynamic study, it was concluded that this temperature range favours fullerene formation (see Chapter 3).

Therefore, argon-helium plasma is able to generate high temperatures and gaseous carbon concentrations in the reactor zone. Both conditions play a key role in the synthesis of fullerenes as shown in Chapter 3.
In the case of argon plasma, vaporization of large carbon particles is achieved only at 50% in the plasma zone. The other 50% of the particle vaporization should be carried out into the reactor zone. This vaporization pattern observed under argon plasma conditions, avoids producing high concentrations of carbon gas species and the carbon-carbon reactions are not easily attainable.

The operating pressure also affects the residence time of reacting species. Lower operating pressures should result in higher gas expansions and higher velocities, at compared to plasmas at higher pressures. Thus, the residence time of reactive species at lower operating pressure (40 kPa) is expected to be smaller than that of 3.3-ms estimated at higher pressure (66 kPa) for both, argon and argon-helium plasmas.

5.3 Temperature Profile into the Reactor and Quenching Section

An experimental test was performed in order to evaluate the temperature profile into the reactor and quenching section. In this test, no carbonaceous material was fed and therefore, the measured temperatures correspond only to the effect of the plasma gas. The flow rates of the different plasma gas applied in the experimental test are shown in Table 4.1. A plate power of 40 kW and operating pressure of 66 kPa was used during the experiment.

<table>
<thead>
<tr>
<th>Thermocouple</th>
<th>Axial Distance from the Top of the Reactor Z (m)</th>
<th>T (K) (5 min)</th>
<th>T (K) (10 min)</th>
<th>T (K) (15 min)</th>
<th>T (K) Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.34</td>
<td>1620</td>
<td>1620</td>
<td>1630</td>
<td>1620</td>
</tr>
<tr>
<td>2</td>
<td>0.44</td>
<td>1540</td>
<td>1520</td>
<td>1500</td>
<td>1520</td>
</tr>
<tr>
<td>3</td>
<td>0.59</td>
<td>1230</td>
<td>1320</td>
<td>1270</td>
<td>1270</td>
</tr>
<tr>
<td>4</td>
<td>0.79</td>
<td>1160</td>
<td>1170</td>
<td>1150</td>
<td>1160</td>
</tr>
</tbody>
</table>
Four $K$-type thermocouples were installed in the experimental system. The thermocouples were placed in such a way that their ends were localized in the center of the reactor. The temperatures were measured by time intervals of 5 minutes from the beginning of the test. Table 5.5 shows the axial position of thermocouples from the top of the reactor (exit of the plasma torch) along with the measured temperatures. Table 5.5 also shows the average temperature for each thermocouple after 15 minutes.

In Figure 5.1, the exit plane of the torch nozzle is placed about 0.15 m from the top of the torch. Using the modelization results of Figure 5.5, it is possible to estimate gas temperatures in the mainstream of the plasma from the exit of the nozzle (0.15 m) to 0.25 m. It is important to remark that, in this study, the exit of the torch nozzle (0.15 m) is the top of the reactor (0.0 m). Table 5.6 shows the estimated gas temperatures in terms of the axial distance from the top of the reactor.

**Table 5.6** Gas Temperatures in the Mainstream of the Plasma Estimated by Modelization

<table>
<thead>
<tr>
<th>Axial Distance from the Top of the Reactor Z (m)</th>
<th>Estimated Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>8980</td>
</tr>
<tr>
<td>0.01</td>
<td>9100</td>
</tr>
<tr>
<td>0.02</td>
<td>9100</td>
</tr>
<tr>
<td>0.03</td>
<td>9000</td>
</tr>
<tr>
<td>0.04</td>
<td>8950</td>
</tr>
<tr>
<td>0.05</td>
<td>8840</td>
</tr>
<tr>
<td>0.06</td>
<td>8670</td>
</tr>
<tr>
<td>0.07</td>
<td>8500</td>
</tr>
<tr>
<td>0.08</td>
<td>8300</td>
</tr>
<tr>
<td>0.09</td>
<td>8100</td>
</tr>
<tr>
<td>0.10</td>
<td>7900</td>
</tr>
</tbody>
</table>

Figure 5.6 depicts the temperature profile for the gas mainstream along the reactor and quenching section. The plot includes the estimated temperatures (by modelization) for the top
of the reactor and the temperatures measured by the thermocouples in the bottom of the reactor and the quenching section.

An exponential fitting was also carried out in order to estimated the gas temperature in the reactor zone. The exponential equation is shown in equation 5.15. The correlation coefficient (r) and the standard error were estimated to be about 0.95 and 720.

\[ T = 9649.9 e^{-3.307Z} \]

(5.15)

![Temperature Profile](image)

Figure 5.6 Temperature Profile Along the Reactor and Quenching Section

The results allow estimating the reactor zone in which fullerenes are mainly synthesized. For example, thermodynamic study developed in Chapter 3 showed that the temperature range for fullerene formation is from 2250 to 3800 K. Using equation 5.1, 3800 K is found at axial
distance of 0.28 m from the top of the reactor, while 2250 K is found at 0.45 m. It means a $\Delta Z$ of about 0.17 m for the formation of fullerenes. Furthermore, if the gas axial velocity estimated in 5.1.2 remains constant (58 m/s) along the reactor, the residence time of the carbon gaseous species is about 3 ms in the zone of fullerene formation. According to kinetic study (see Chapter 3), the reaction time for fullerene formation was estimated to be smaller than 1 ms. Therefore, a residence time of 3 ms is sufficient for fullerene formation. It might be speculated that, in the remaining time, carbon species might react to growth fullerene structures or simply increase fullerene concentration.

At this point, it is important to observe that the evaluation of the residence time in the zone of fullerene formation assumes axial flux. Turbulent conditions along recirculation and temperature and velocity gradients might also produce a significant effect on the residence time.

In addition, the analysis of the residence time of carbon species also considers that all carbon species are in gas phase. In other words, the analysis does not take into account the effect of gas cooling due to the particle vaporization, which also showed to play a key role during the fullerene formation.

Although this analysis does not constitute conclusive proof of the residence time of the carbon gaseous species into the zone of fullerene formation, the results might be considered satisfactory for the purpose of this study.
CHAPTER 6  EXPERIMENTAL RESULTS AND DISCUSSION ON
FULLERENE SYNTHESIS

This chapter describes the methodology and the experimental results obtained in this work. The results are presented in a defined order beginning with the preliminary experimental work followed by results obtained in the statistical experimental design. Theoretical models and assumptions are verified and correlated with experimental data throughout the chapter.

6.1 Preliminary Experimental Results

Table 6.1 summarized the operating conditions used during the preliminary tests.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Catalyst (g/min)</th>
<th>Raw Material Feed Rate</th>
<th>Run Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2 (Fe)</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>7.5 slpm (C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>1.5 slpm (C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>1.2 (Fe)</td>
<td>8.0 slpm (C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>1.5 (Fe)</td>
<td>2.0 slpm (C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>1.5 (Co:Ni)</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>1.5 (Co:Ni)</td>
<td>8.0 slpm (C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>2.4 (Co:Ni)</td>
<td>2.0 slpm (C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>0.24 (Fe)</td>
<td>0.3 g/min (CB)</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.9 g/min (CB)</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>1.5 (Fe)</td>
<td>1.9 g/min (CB)</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>0.52 (Fe)</td>
<td>1.3 g/min (CB)</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
<td>0.6 g/min (CB)</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
<td>12 ml/min (C&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>5</td>
</tr>
</tbody>
</table>
In all carbon vaporization tests performed, a very light soot-like product was found deposited on the reactor walls. When acetylene was used as raw material, flying soot threads falling down into the reactor were observed. The plasma color also varied during the experiments, and depended on the type of catalyst used. For example, a green color was observed for Fe while blue color was observed for the Co-Ni mixture.

Table 6.2 shows the experimental results in terms of C_{60} content along with the mass balance for each test. The mass balance is defined in terms of percent-recovered mass according to the equation 6.1. Differences of the 100% in the mass balance can be explained by the fact that carbon was lost as C_{2}H_{2}, CH_{4} and C_{2}H_{4}. Although this finding was not experimentally verified, thermodynamic equilibrium calculations (see Chapter 3) showed that these species might be the main compounds of the exhaust gas. A portion of the soot rested also attached to the experimental equipment walls and another part was released to the environment during the soot recovering process.

The results show that C_{60} was preferably formed when carbon black and C_{2}Cl_{4} were used as raw materials. Non-C_{60} content was found during the tests using C_{2}H_{2}. These findings are correlated with the thermodynamic equilibrium state present under plasma conditions. For example, using acetylene as raw material (tests 2 - 8), the thermodynamic study developed in Chapter 3 indicates that fullerenes are formed in the temperature range from 2200 to 3800 K.

\[
\text{Recovered Mass (\%) = } \frac{\text{Recovered Soot Mass}}{\text{Feeding Carbon and Catalyst Mass}} \times 100
\] (6.1)

However, in this temperature range the concentrations of C_{2}H_{2}, CH_{4} and C_{2}H_{4} and the radical species H, CH, C_{2}H and C_{3}H are also quite significant. The hydrogen and the small hydrocarbon radicals become competition species for the C_{2} and C_{3} precursor molecules. This phenomenon inhibits fullerene growth.
TABLE 6.2  CARBON MASS BALANCE AND C₆₀ CONCENTRATION FOR THE PRELIMINARY EXPERIMENTAL RESULTS

<table>
<thead>
<tr>
<th>Test N.</th>
<th>Recovered Mass (%</th>
<th>Fullerene Content (% wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>93.7</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>76.3</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>89.7</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>67.7</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>72.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>97.9</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>71.8</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>63.4</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>80.0</td>
<td>3.6</td>
</tr>
<tr>
<td>10</td>
<td>41.7*</td>
<td>0.1</td>
</tr>
<tr>
<td>11</td>
<td>87.3</td>
<td>0.0</td>
</tr>
<tr>
<td>12</td>
<td>92.6</td>
<td>0.1</td>
</tr>
<tr>
<td>13</td>
<td>74.6</td>
<td>1.6</td>
</tr>
<tr>
<td>14</td>
<td>87.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

* Leak in the system

In contrast, when carbon black was used as raw material (tests 9 to 13), the carbon vapor pressure inside the plasma reactor was increased. This favours carbon-carbon reactions and fullerene formation was easier to achieve (see Chapter 3).

A high C₆₀ concentration was also observed when C₂Cl₄ was used as raw material (test 14). This result showed that the use of a liquid starting material with smaller bond dissociation energy (397 kJ/mol for C - Cl and 607 kJ/mol for C - C) improves the vaporization process and increases the carbon vapor pressure inside the reactor, which favours fullerene formation.

During the C₆₀ analysis by UV-spectrometry, the soot extraction of this sample showed a strong brown-red color. This color can be related to the synthesis of some chlororganic compounds. A high performance liquid chromatography (HPLC) analysis was also carried out in order to avoid any over estimation on the C₆₀ concentration. Although HPLC is a powerful characterization technique for quantitative analysis of fullerenes, in this study it was used only qualitatively in order to evaluate the likely formation of chlororganic by-products. Figure 6.1 depicts the soot extraction chromatogram while the Table 6.3 shows the retention times and the percent area for the different compounds.
The results show that not only C\textsubscript{60} fullerene (peak 5) was synthesized, but also C\textsubscript{70} (peak 8). Various unknown peaks (1, 2, 3, 4, 6, 7 and 9) were also observed in the chromatogram. These peaks might be related with some chlororganic compounds synthesized during the test. Similar results were found by Alexakis (1997) during fullerene synthesis in a D.C. plasma system using C\textsubscript{2}Cl\textsubscript{4} as starting material. C\textsubscript{6}Cl\textsubscript{6} (MW=284), C\textsubscript{8}Cl\textsubscript{8} (MW=308), C\textsubscript{10}H\textsubscript{8} (MW=404), C\textsubscript{12}Cl\textsubscript{8} (MW=547), C\textsubscript{14}Cl\textsubscript{8} (MW=452) and C\textsubscript{18}Cl\textsubscript{10} (MW=547) were identified by GC-MS analyses in samples of fullerene soot collected in the quenching zone.

Xie et al., (2001) also synthesized chlorinated organic compounds via glow discharge reaction using chloroform as raw material. Chlorinated aromatic molecules ranged from C\textsubscript{6}Cl\textsubscript{6} to C\textsubscript{50}Cl\textsubscript{12}. According to Xie’s results as well of Figure 6.1 of this work, the relative abundance of the chlororganic products seems to be reduced with the increase of their carbon atoms.
This finding suggests that, under highly concentrate chlorine atmosphere, the fullerene growth process may be analogous to the polycyclic aromatic hydrocarbon growth (Pope et al. 1993) shown in Chapter 2.

<table>
<thead>
<tr>
<th>Peak N</th>
<th>Retention Time (min)</th>
<th>Peak Area (%)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.03</td>
<td>2.82</td>
<td>chlororganic</td>
</tr>
<tr>
<td>2</td>
<td>3.88</td>
<td>2.86</td>
<td>chlororganic</td>
</tr>
<tr>
<td>3</td>
<td>4.97</td>
<td>4.42</td>
<td>chlororganic</td>
</tr>
<tr>
<td>4</td>
<td>6.23</td>
<td>6.58</td>
<td>chlororganic</td>
</tr>
<tr>
<td>5</td>
<td>7.25</td>
<td>49.99</td>
<td>C_{60}</td>
</tr>
<tr>
<td>6</td>
<td>7.85</td>
<td>1.94</td>
<td>chlororganic</td>
</tr>
<tr>
<td>7</td>
<td>10.45</td>
<td>19.37</td>
<td>chlororganic</td>
</tr>
<tr>
<td>8</td>
<td>12.37</td>
<td>6.74</td>
<td>C_{70}</td>
</tr>
<tr>
<td>9</td>
<td>14.73</td>
<td>2.23</td>
<td>chlororganic</td>
</tr>
</tbody>
</table>

Tirey et al., (1990) studied the formation kinetic of perchlorinated olefinic and aromatic species during the pyrolysis of C_{2}Cl_{4}. They showed that the formation of higher molecular weight aromatic species is similar to its non-chlorinated analogous (hydrocarbons). They suggested that olefinic and acetylenic species such as C_{2}Cl_{3} and C_{2}Cl_{2} play a key role in the chloroaromatic molecular growth.

As explained in Chapter 4, although the C_{2}Cl_{4} degradation test showed a high yield of fullerenes, all tests with this compound were abandoned. One of the main reasons was the difficulty to systemically identify fullerenes and chlororganic by-products using simple UV spectrophotometric analysis.

Thus, all the tests of the experimental design were carried out using carbon black as raw material. Tests 9 and 13 also showed relatively high fullerene yield.

Figures 6.2 and 6.3 show Scanning Electron Microscopy (SEM) micrographs of a specific type of carbon encapsulation found in the fullerene soot produced in test 9. In this encapsulation, the inner-core of unreacted particle is partially surrounded by carbon nano and
microparticles and also carbon nanofibers. This particle, which survived the plasma conditions without evaporation, is covered with some spaghetti-like nanofibers. In terms of their outer diameters (20-50 nm), the nanofibers may be considered as carbon nanotubes but further analyses by transmission microscopy are required to confirm this finding. According to micrographs, it was speculated that the carbon layer around particle might be formed via thermo and photophoresis mechanisms. The effects of these mechanisms on the carbon particles migration will be explain in detail later in this chapter. In a first approximation, the micrographs also suggest that the growth might occur via the gaseous carbon adsorption by the particle surface followed by the carbon species dissolution and diffusion through the active sites, their precipitation to form the carbon fiber body and the migration of the remaining carbon species around the particle surface to form the fiber skin component. However, the superposition of fibre might be also the result of some kind of carbon deposition phenomena.

Figure 6.2 SEM Micrograph of an Unreacted Metallic Particle Surrounded by Carbon Layers Produced by Vaporization of a Carbon Black – Fe Mixture
A high density of carbon nanoparticles was also found associated with the nanofibers. Their diameters ranged from 5 to 40 nm. These carbon nanoparticles may be also linked with the formation of giant fullerenes as it will be shown later in Chapter 7.
No carbonaceous material was fed into the system in tests one and six in order to evaluate the plasma effect on the vaporization process of catalyst. The main effect was an increase in the catalyst's surface area after the plasma treatment.

Normally, iron particles changed from 0.9 to 16.2 m²/g whereas nickel changed from 0.6 to 15.1 m²/g. These changes in the surface area of particles indicate an overall decrease in the particle size as shown in Figures 6.4 and 6.5.

Although Figure 6.4 shows that catalyst vaporization was effective, some catalyst particles can survive to vaporization as it can be seen in Figure 6.5. This finding agrees with the particle vaporization study performed in Chapter 4. Specifically, Figure 6.5 shows that most of the agglomerates of Co-Ni particles were well vaporized producing finer agglomerates, but a catalyst particle also survived to plasma conditions.

Figure 6.4  SEM Image of Iron Particles Used as Catalyst Before and After Plasma Treatment

Figure 6.5  SEM Image of Co:Ni Mixture Used as Catalyst Before and After Plasma Treatment
6.2  Statistical Experimental Design Results

Two different approaches have been used to interpret the results of the experimental work. The first approach statistically evaluates the effect of the operating parameters on the synthesized C_{60} concentration. The second evaluates the experimental results in terms of the physical and chemical phenomena's involved during the carbon particle vaporization.

6.2.1  Statistical Analysis of Results

This experimental part was performed according to the statistical experimental design discussed in Chapter 4. The response variable was the C_{60} concentration, which was measured via UV spectrometric analysis. Table 6.4 summarizes the experimental results in terms of recovered mass calculated by equation 6.1 and C_{60} concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ident.</th>
<th>Reactor Pressure (kPa)</th>
<th>Feed Rate (g/min)</th>
<th>Catalyst Ratio (% mol)</th>
<th>Plate Power (kW)</th>
<th>Recovered Mass (%)</th>
<th>C_{60} Concentration (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>CB07</td>
<td>40</td>
<td>1.3</td>
<td>2</td>
<td>40</td>
<td>72.6</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>CB08</td>
<td>66</td>
<td>1.9</td>
<td>2</td>
<td>40</td>
<td>85.1</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>CB14</td>
<td>40</td>
<td>7.6</td>
<td>2</td>
<td>20</td>
<td>83.1</td>
<td>0.0</td>
</tr>
<tr>
<td>16</td>
<td>CB15</td>
<td>66</td>
<td>6.0</td>
<td>2</td>
<td>20</td>
<td>88.6</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>CB16</td>
<td>40</td>
<td>2.0</td>
<td>2</td>
<td>20</td>
<td>73.7</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>CB17</td>
<td>66</td>
<td>2.0</td>
<td>2</td>
<td>20</td>
<td>78.6</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>CB18</td>
<td>40</td>
<td>4.6</td>
<td>2</td>
<td>40</td>
<td>90.3</td>
<td>0.1</td>
</tr>
<tr>
<td>15</td>
<td>CB19</td>
<td>66</td>
<td>4.6</td>
<td>2</td>
<td>40</td>
<td>79.6</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>CB22</td>
<td>40</td>
<td>2.0</td>
<td>4</td>
<td>20</td>
<td>45.9*</td>
<td>0.0</td>
</tr>
<tr>
<td>12</td>
<td>CB23</td>
<td>66</td>
<td>1.6</td>
<td>4</td>
<td>20</td>
<td>44.9*</td>
<td>0.0</td>
</tr>
<tr>
<td>11</td>
<td>CB25</td>
<td>40</td>
<td>4.2</td>
<td>4</td>
<td>20</td>
<td>73.3</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>CB28</td>
<td>40</td>
<td>3.3</td>
<td>4</td>
<td>40</td>
<td>84.5</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>CB29</td>
<td>40</td>
<td>2.3</td>
<td>4</td>
<td>40</td>
<td>91.6</td>
<td>0.3</td>
</tr>
<tr>
<td>13</td>
<td>CB30</td>
<td>66</td>
<td>3.7</td>
<td>4</td>
<td>40</td>
<td>87.6</td>
<td>0.4</td>
</tr>
<tr>
<td>14</td>
<td>CB31</td>
<td>66</td>
<td>2.5</td>
<td>4</td>
<td>40</td>
<td>90.8</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>CB32</td>
<td>66</td>
<td>2.6</td>
<td>4</td>
<td>20</td>
<td>93.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* Leak in the system
It is important to remark the differences between the proposed feed rate (2 and 4 g/min) and the real feed rate, which is shown in column 3. These differences were mainly due to the difficulty in accurately controlling the powder feeder screw speed. The nanometric size of the carbon black tends to agglomerate with the nickel catalyst forming particles with a wide size distribution as shown in Table 5.2. This large difference on particle size caused variations in the powder feed rate.

The statistical computations were performed with the computer software Design-Expert, version 6.0.1 (2000) from Stat-Ease, Inc.

In any statistical study, the estimation of the effects and the analysis of variance are important. These tools help to determine which factors and factor interactions have a statistically important effect on the response variable. According to the estimations of the effects shown in Table 6.5, the main factors A (reactor pressure), B (feed rate) and D (plate power), and the interactions BD (feed rate-plate power) and CD (composition-plate power) have the strongest influence on the C_{60} content.

**TABLE 6.5 EFFECTS LIST SHOWING THE FACTORS AND INTERACTIONS WITH HIGHEST INFLUENCE ON THE C_{60} CONTENT**

<table>
<thead>
<tr>
<th>Term</th>
<th>Effect</th>
<th>Sum of Squares</th>
<th>% Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.2819</td>
<td>0.3359</td>
<td>7.5686         *</td>
</tr>
<tr>
<td>B</td>
<td>-0.3113</td>
<td>0.4971</td>
<td>11.2019        *</td>
</tr>
<tr>
<td>C</td>
<td>-0.1906</td>
<td>0.1902</td>
<td>4.2868</td>
</tr>
<tr>
<td>D</td>
<td>0.4891</td>
<td>1.0196</td>
<td>22.9768        *</td>
</tr>
<tr>
<td>AB</td>
<td>-0.1920</td>
<td>0.2118</td>
<td>4.7733</td>
</tr>
<tr>
<td>AC</td>
<td>-0.0781</td>
<td>0.0381</td>
<td>0.8581</td>
</tr>
<tr>
<td>AD</td>
<td>0.1358</td>
<td>0.0988</td>
<td>2.2271</td>
</tr>
<tr>
<td>BC</td>
<td>0.1029</td>
<td>0.0356</td>
<td>0.8018</td>
</tr>
<tr>
<td>BD</td>
<td>-0.5133</td>
<td>0.9013</td>
<td>20.311         *</td>
</tr>
<tr>
<td>CD</td>
<td>-0.2959</td>
<td>0.3733</td>
<td>8.4128         *</td>
</tr>
<tr>
<td>ABC</td>
<td>0.1629</td>
<td>0.0697</td>
<td>1.5708</td>
</tr>
<tr>
<td>ABD</td>
<td>-0.2839</td>
<td>0.2165</td>
<td>4.8787</td>
</tr>
<tr>
<td>ACD</td>
<td>-0.2821</td>
<td>0.3643</td>
<td>8.2098</td>
</tr>
<tr>
<td>BCD</td>
<td>0.0485</td>
<td>0.0100</td>
<td>0.2261</td>
</tr>
</tbody>
</table>
Table 6.6 shows the analysis of variance including the main factors A, B, C and D and the interactions BD and CD. The main factor C does not present a strong influence on the C_{60} content. However, it was also included in order to hierarchy the statistical model.

**Table 6.6  ANALYSIS OF VARIANCE FOR THE FACTORS AND INTERACTIONS WITH HIGHEST INFLUENCE ON THE C_{60} CONTENT**

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F_o</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>3.34</td>
<td>6</td>
<td>0.56</td>
<td>4.54</td>
<td>0.0216</td>
</tr>
<tr>
<td>A</td>
<td>0.66</td>
<td>1</td>
<td>0.66</td>
<td>5.40</td>
<td>0.0453</td>
</tr>
<tr>
<td>B</td>
<td>0.88</td>
<td>1</td>
<td>0.88</td>
<td>7.20</td>
<td>0.0249</td>
</tr>
<tr>
<td>C</td>
<td>0.048</td>
<td>1</td>
<td>0.048</td>
<td>0.39</td>
<td>0.5464</td>
</tr>
<tr>
<td>D</td>
<td>1.31</td>
<td>1</td>
<td>1.31</td>
<td>10.70</td>
<td>0.0097</td>
</tr>
<tr>
<td>BD</td>
<td>1.12</td>
<td>1</td>
<td>1.12</td>
<td>9.14</td>
<td>0.0144</td>
</tr>
<tr>
<td>CD</td>
<td>0.40</td>
<td>1</td>
<td>0.40</td>
<td>3.30</td>
<td>0.1027</td>
</tr>
<tr>
<td>Residual</td>
<td>1.10</td>
<td>9</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>4.44</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The final equation to estimate the C_{60} content, in terms of the coded factors, can be written according to the equation 6.2.

\[
C_{60} = 0.37 + 0.20A - 0.17B - 0.058C + 0.29D - 0.20BD - 0.17CD
\]  \hspace{1cm} (6.2)

The analysis of the model residuals, which were calculated as the difference between the experimental and estimated C_{60} content, revealed that the normality assumptions of the statistical study were satisfied. Here, values of the estimated C_{60} concentrations were computed using equation 6.2.
6.2.2 High Performance Liquid Chromatography Analysis

Such as the case of $C_2Cl_4$ treatment, a high performance liquid chromatography (HPLC) analysis was also carried out in order to verify the possible synthesis of unknown graphitic structures. Such structures may be able to absorb UV light producing erroneous results when analyzed by UV spectrophotometry. It is important to remark that toluene extractions of the fullerenic soot showed a clear purple color characteristic of $C_{60}$ solutions.

![Image](image.png)

Figure 6.6 Typical HPLC-UV Chromatogram of a Soot Produced Using Carbon Black – Nickel Mixture as Raw Material

HPLC results showed that, just like the preliminary test using $C_2Cl_4$ as starting material, $C_{70}$ fullerene was also synthesized. A typical soot toluene extraction chromatogram is depicted in Figure 6.6. Table 6.7 shows the corresponding compound peak areas and retention times.
<table>
<thead>
<tr>
<th>Peak N</th>
<th>Retention Time (min)</th>
<th>Peak Area (%)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.40</td>
<td>92</td>
<td>C₆₀</td>
</tr>
<tr>
<td>2</td>
<td>8.28</td>
<td>0.83</td>
<td>unknown</td>
</tr>
<tr>
<td>3</td>
<td>12.33</td>
<td>7.05</td>
<td>C₇₀</td>
</tr>
</tbody>
</table>

The relative C₇₀ concentration produced using CB-Ni mixture is smaller than that of C₂Cl₄. In fact, when C₂Cl₄ was used as starting material the C₇₀/C₆₀ ratio (0.13) was about 1.7 times higher than that produced with CB-Ni mixture (0.08). This finding might be related with the use of a liquid carbonaceous starting material such as C₂Cl₄. A liquid material allows higher throughputs than the solid CB-Ni mixture. In this way, the carbon vapor pressure is increased and fullerene growth is favoured. Additionally, in the fullerene synthesis using chlororganic materials, small carbon clusters are produced in the plasma. Because chlorine atoms saturate the dangling bonds of these clusters, the growth of fullerenes might be carried out via a sequential addition of C₂Cl₂ specie followed by the subtraction of a chlorine atom (Xie et al., 2001), similar to the growth of polyaromatic hydrocarbons. In contrast, when using pure carbon as starting material, the small carbon clusters do not present dangling bonds and their growth is stopped before they reach larger fullerenic structures.

An unknown extractable compound was also identified between the C₆₀ and C₇₀ peaks. Although this peak may be the result of any extractable graphitic molecule possessing between 60 and 70 carbon atoms, its relative concentration is quite small and does not influence the final result of the fullerene content. Additionally, further and different analyses are required to characterize this structure.

Thus, it is concluded that the results obtained from the UV spectrophotometric analyses might be used as indication of the fullerene content.
6.2.3 Plasma Emission Spectroscopy

Optical emission measurements of the Swan band (0-0) emitted by \( \text{C}_2 \) radicals were carried out to characterize the overall temperature and column density during the vaporization process.

The optical system used for plasma measurements was described in detail in Chapter 4 where an example of the experimental normalized intensity distribution in the \( \text{C}_2 \) band was presented. The overall temperatures were estimated using the spectra fitting method and Boltzmann plot. In the case of significant self-absorption, both methods lead to temperature differences of few hundred degrees (Lange et al., 1999 and Huczko et al., 2000). Therefore, the temperatures reported here were the mean values of both methods, as Lange and Huczko usually do it.

At this point, it must be admitted that the measured temperatures only represent overall temperatures of the particle vaporization process. These temperatures were estimated using the light intensity received by the achromatic lens in its focal point from the whole plasma tail. The temperature measurements were carried out in order to compare qualitatively the vaporization process of the tests at different operating conditions, as shown later.

The measured overall temperatures were average estimated values.

Several optical measurements were obtained in 0.2-min time intervals during the beginning of the experimental test.

Figures 6.7 and 6.8 show two representative examples of overall temperatures and \( \text{C}_2 \) column densities for experimental tests performed at 40 and 20 kW, respectively.

It can be seen that, at the beginning of the tests, the plasma temperature and column density significantly decrease and vary lengthwise the run time. This observation is more clearly emphasized during the test carried out at 20 kW (see Figure 6.8).
The phenomena might be explained considering the unsteady state cooling process during the injection of raw material particles. In other words, in this initial stage the plasma is cooled due to feeding of the raw material. From the figures, it is inferred that the steady state condition might be reached about 1.2 min for the test performed at 40 kW and about 1.5 min for the test at 20 kW. Additionally, a periodic peak is observed in the figures, for example in Fig. 6.8 a periodic peak appears at about 1 min. This peak is the result of feeding processus of raw material. Because raw material is not fed continuously, variations in the spectroscopic measurement are observed.

Based on an average run time of 10 min, it might be established that all the experimental tests were performed under steady state conditions.
Figure 6.8  Plasma Temperature and C₂ Column Density for the Test CB32 at 20 kW of Plate Power

Table 6.8 summarizes the estimated overall temperature and C₂ radical column density of the last five tests.

As expected, the test carried out at lower plate power (20 kW) had the lowest measured overall temperature.

<table>
<thead>
<tr>
<th>Test</th>
<th>Plasma Temperature (K)</th>
<th>Column Density, x 10^{15} (cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB28</td>
<td>4150</td>
<td>0.16</td>
</tr>
<tr>
<td>CB29</td>
<td>4900</td>
<td>3.20</td>
</tr>
<tr>
<td>CB30</td>
<td>5150</td>
<td>2.60</td>
</tr>
<tr>
<td>CB31</td>
<td>4500</td>
<td>0.80</td>
</tr>
<tr>
<td>CB32</td>
<td>3650</td>
<td>2.50</td>
</tr>
</tbody>
</table>
6.3 Effect of the Operating Parameters on the Fullerene Yield

As indicated above, the results of the statistical study revealed that the operating pressure, plate power and raw material feed rate present the higher effects on the fullerene yield.

6.3.1 Effect of the Operating Pressure

The analysis of the main factor influence on the response variable revealed that the reactor pressure (factor A) has a positive effect on the C_{60} content. In other words, higher C_{60} concentrations were produced at higher (66 kPa) than at lower operating pressure (40 kPa). The increase in the reactor pressure caused an increase of 0.4 %wt in the C_{60} content. Since the maximum C_{60} concentration of all the tests was 2.1 %wt, a 0.4 %wt means an overall increase in the production rate of 20 %.

This behavior might be explained by the larger residence time experimented by carbon particles and species in the zone of high temperature when operated at high pressures. As explained in Chapter 4, higher operating pressures result in lower gas expansions and velocities, as compared to plasmas at lower pressures.

The results of the emission spectrometric measurements can be used to corroborate this finding. These results are shown in Table 6.8. The estimated overall temperature of the vaporization process for the tests CB28 (40 kPa) can be compared with that of the test CB30 (66 kPa). Both tests were carried out at the same conditions of plate power (40 kW) and carbon feed rate (4 g/min). The test CB30 presents a higher overall temperature (5150 K) than test CB28 (4150 K). More efficient particle vaporization is reached in test CB30 thanks to the higher residence time of the particle in the hot zones of the plasma. In this study, the Swan band emitted by the C_2 radicals was used to determine the overall temperature of the vaporization process. Thus, higher emissions are produced at higher carbon vaporization rates.

Additionally, in the mathematical model results showed in Chapter 4, helium plasma at 66 kPa presents an estimated average temperature of 7500 K, velocity of 58 m/s and residence time for of 3.3 ms. Under these conditions, the study of the particle vaporization showed that particles of 100 µm can be completely vaporized into the plasma tail. Because the high
temperature of the plasma tail, temperatures between 2250 and 3800 K are usually found in the reactor zone as shown in Chapter 5. Thermodynamic study showed that this temperature range favours fullerene synthesis. Thermodynamics also showed that the use of low pressure inside the plasma reactor affects the fullerene formation. At low pressures, the formation of small carbon clusters such as $C_2$ and $C_3$ are favoured while equilibrium concentrations of fullerenes are reduced.

In contrast, thermodynamics showed that the increase of the system pressure slightly enhances fullerene equilibrium concentration. In other words, the use of higher pressures improves fullerene production due to the reduction of the equilibrium concentrations of the small carbon clusters.

Therefore, the experimental results in which lower fullerene yields are synthesized at low pressures and higher yields are produced at higher pressures, agree with thermodynamic results.

Additionally, the kinetic study showed that the estimated reaction time for fullerene formation is smaller than 1 ms. Taking into account the lower expansion rates of the plasma gas at high pressures, carbon species have quite enough time to react. In fact, in Chapter 5, a residence time of 3 ms was estimated in the zone of fullerene formation (2250 – 3800 K). Therefore, it might be concluded that a high operating pressure increases the residence time of the particles inside the plasma tail favouring their complete vaporization. Furthermore, high pressures also increase the residence time of the gaseous carbon species in the hot zones of the reactor. This high residence time enhances carbon-carbon reactions involved in the fullerene formation.

6.3.2 Effect of the Plate Power

Similar behavior was also observed in the effect of the plate power (factor D). An increase of 1.3 %wt in the $C_{60}$ content was reached when the plate power was increased from 20 to 40 kW. This increase in yield is a gain of approximately 60 %.

As expected, higher plate powers produce higher plasma temperatures. In the Table 6.8, tests CB31 and CB32 were carried out at 40 and 20 kW, respectively and, at the same conditions of
pressure (66 kPa) and particle feed rate (2 g/min). It is clear that at 20 kW (CB32) a lower overall temperature of the vaporization process was reached (3650 K). In contrast, at 40 kW (CB31), a higher overall temperature was measured (4500 K). Higher power inputs favour the ionization, collision and recombination processes of the plasma species, which increase the kinetic temperature of the plasma. Higher power inputs also enhance the vaporization of carbon particle and the formation of C₂ radicals, which were used to estimate the overall temperature of the process.

In the vaporization study of the Chapter 5, the higher average plasma temperature (7500 K) showed in the Table 5.4 represents the higher plasma power inputs. In contrast with low power inputs in which only particles of about 50 μm are vaporized, high power inputs are able to completely vaporize until 100-μm particles. Higher plate powers also allow maintaining high temperature profiles in the reaction zone. As indicated above, a high temperature enhances fullerene formation.

The kinetic study showed that, at high temperature, carbon reaction rates are accelerated. A high temperature strongly enhances the yield of carbon species C and C₃, which are considered to be fullerene precursors.

Kinetic results also showed that a high reaction temperature enhances the fullerene formation via the sequential addition of C₂ and C₃ precursors. Chapter 5 showed that argon-helium plasma at 40 kW presents temperatures higher than 2250 K in the reactor zone. According to kinetics, above 2000 K, the fullerene growth is not only carried out via C₂ species, but also by reactions of C₃ species. These high temperatures also prevent the formation of planar graphitic structures.

Therefore, the use of higher plate power impacts positively the synthesis of fullerenes owing to high plate powers generate high temperatures in the plasma tail and into the reactor zone. High plasma temperatures increase particle vaporization inside the plasma tail while high reactor temperature favours fullerenes growth.
6.3.3 Effect of the Raw Material Feed Rate

In contrast with operating pressure and plate power, the increase of the raw material feed rate had a negative effect on the C$_{60}$ content. A decrease of 0.7 %wt of C$_{60}$, which corresponds to a loss of 33 %, was observed when the feed rate was increased from 2 to 4 g/min. According to the thermodynamic study, an increase in the carbon feed rate enhances the carbon vapor pressure inside the plasma reactor and slightly extends the temperature range in which the fullerene formation is carried out. In fact, the kinetic study showed that the reaction rate of the C compounds is accelerated when a high solid carbon concentration is used as starting material. Thus, the formation of fullerene structures via C$_2$ and C$_3$ precursors should have been enhanced under high carbon concentration conditions. In other words, high raw material feed rate should have favoured fullerene production.

Therefore, this negative effect might be explained by a poor vaporization of the raw material particles.

This finding can be explained by comparing the temperature of the tests CB28 at 3.3 g/min (4150 K) and CB29 at 2.3 g/min (4900 K). These tests were performed at the same reactor pressure (40 kPa) and plate power (40 kW). The higher temperature measured in test CB29 indicates that carbon particles might have been better vaporized at lower feed rate. Higher light intensity might be detected when higher C$_2$ radical concentrations are produced. When higher feed rate was used, the overall plasma temperature was decreased because the high-energy requirements to sublime carbon particles and heat gaseous species.

The particle vaporization study showed that lower plasma temperatures always involve small vaporization yield of the carbon particles. Additionally, the kinetic study also showed that lower fullerene yields are produced at lower temperatures.

The effect of the plate power on the poor particle vaporization and, as consequence, the low fullerene yield can be also analyzed through the interactions between the feed rate and the catalyst ratio.
The variation of the $C_{60}$ content as a function of the interaction between the plate power and the feed rate factors is represented in the Table 6.9. Reactor pressure was maintained in 66 kPa and the catalyst ratio in 2%.

**TABLE 6.9 INTERACTION BETWEEN PLATE POWER AND FEED RATE FACTORS**

<table>
<thead>
<tr>
<th>Plate Power (kW)</th>
<th>Feed Rate (g/min)</th>
<th>$C_{60}$ Content (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2</td>
<td>0.14</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>0.19</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td>1.45</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
<td>0.72</td>
</tr>
</tbody>
</table>

The highest interaction effect occurs when the plate power is at the higher level (40 kW) and when the raw material feed rate is at the lower level (2 g/min). This combination favours the vaporization process of the particles and the carbon-carbon reactions at high temperature. In contrast, the smallest effect is found at 20 kW and 2 g/min, i.e. at low plate power and feed rate levels.

The interaction between the plate power and the catalyst ratio had also a statistically significant effect on $C_{60}$ yield when high plate power and low catalyst ratio are used. The weakest effect occurs at low plate power and catalyst ratio levels (20 kW and 2%) as shown in Table 6.10.

**TABLE 6.10 INTERACTION BETWEEN PLATE POWER AND CATALYST RATIO**

<table>
<thead>
<tr>
<th>Plate Power (kW)</th>
<th>Catalyst Ratio (% mol)</th>
<th>$C_{60}$ Content (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2</td>
<td>0.14</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>0.36</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td>1.45</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Thus, the optimal operating conditions for fullerenes synthesis can be established as shown in Table 6.11.

Three additional tests were also carried out. The first was a corroboration test to verify the process repeatability and the last two tests were carried out using pure argon as plasma gas.

**TABLE 6.11  OPTIMAL OPERATING CONDITIONS**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Level</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Pressure</td>
<td>High</td>
<td>66 kPa</td>
</tr>
<tr>
<td>Feed Rate</td>
<td>Low</td>
<td>2 g/min</td>
</tr>
<tr>
<td>Catalyst Ratio</td>
<td>Low</td>
<td>2 %mol</td>
</tr>
<tr>
<td>Plate Power</td>
<td>High</td>
<td>40 kW</td>
</tr>
</tbody>
</table>

Table 6.12 shows the operating conditions used in these tests and the experimental results in terms of the recovered mass and C<sub>60</sub> concentration. The corroboration test operating conditions were based on the experimental design test in which the highest C<sub>60</sub> content was obtained (run 2, CB08). The same plasma gas flows showed in Table 4.1 were used. The argon tests were carried out using 90 slpm for sheath, 25 slpm for central and 11 slpm for powder plasma gas. These tests were performed to evaluate the Argon plasma gas effect on the fullerene synthesis. Argon is an obligatory plasma gas that must be used to assure the radio frequency plasma torch stability when a high plate power is used.

**TABLE 6.12  ADDITIONAL CORROBORATION TESTS**

<table>
<thead>
<tr>
<th>Run</th>
<th>Ident.</th>
<th>Plate Power (kW)</th>
<th>Reactor Pressure (kPa)</th>
<th>Feed Rate (g/min)</th>
<th>Catalyst Ratio (%mol)</th>
<th>Time (min)</th>
<th>Recovered Mass (%)</th>
<th>C&lt;sub&gt;60&lt;/sub&gt; Content (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>CB09</td>
<td>40</td>
<td>79</td>
<td>2.0</td>
<td>2</td>
<td>15</td>
<td>91.4</td>
<td>2.0</td>
</tr>
<tr>
<td>18</td>
<td>CB12</td>
<td>20</td>
<td>40</td>
<td>2.1</td>
<td>2</td>
<td>15</td>
<td>99.0</td>
<td>0.0</td>
</tr>
<tr>
<td>19</td>
<td>CB13</td>
<td>40</td>
<td>40</td>
<td>2.0</td>
<td>2</td>
<td>17</td>
<td>91.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>
As expected, the C\textsubscript{60} content synthesized in the repeatability test (run 17, CB09) showed a good agreement with previous tests carried out under similar conditions (run 2, CB08). Runs 18 and 19 showed that argon plasma gas has a negative effect on fullerene synthesis. Poor particle vaporization is the most likely explanation as it was studied in the Chapter 5. Argon plasma has a lower thermal conductivity than helium plasma, which translates to less energy for particle vaporization. Argon plasma presents similar velocities and residence time than helium plasma. However, specific enthalpy and heat transfer of argon plasma are lower than those of helium plasma and large carbon particles are not able to completely vaporize. As consequence, fullerene formation is inhibited because the high carbon vapor pressure necessary in the fullerene formation process is not reached.

6.4 Formation of Carbon Nanostructures

Other characterization techniques were also used in an attempt of better understanding nanostructure formation in the fullerene synthesis by plasma.

6.4.1 Thermogravimetric Analysis

Thermogravimetric analyses were also used for solid product characterization. Figure 6.9 shows the Differential Thermogravimetric (DTG) curves of four different samples analyzed under the TGA procedure described in Chapter 4. The fullerite curve corresponds to the analysis of the as-produced soot from test CB08. C\textsubscript{60} extract curve corresponds to the soot extraction. BP3700 and Nickel curves correspond to the raw material analyses.
Figure 6.9  DTG Curves of a Typical Raw-Soot Sample and Blank Tests

There is a clear relationship between the pure material ($C_{60}$ extract and BP3700) and fullerite peaks.

A small peak at about 300 °C is also observed in the $C_{60}$ extract curve. Shi et al., (2000) showed that the burning temperature of amorphous carbon nanoparticles is about 350 °C. Therefore, this peak might correspond to the combustion of small nanoparticles of amorphous carbon that were not retained during the filtration of the $C_{60}$ extract. Because TGA and HPLC samples were obtained in similar way, it is likely that the unknown structure detected in the HPLC test be produced by the same small nanoparticles of the peak at 300 °C.

Saxby et al. (1992) showed that, at heating rate of 10 °C/min, the temperature of maximum rate of weight loss for $C_{60}$ is about 545 °C. Similar results were reported by Zhang et al. (1997) and Shi et al. (2000) who found temperatures of weight loss about 530 and 568 °C, respectively. As well, Pang et al. (1993) reported a temperature of 695 °C for the weight loss of nanotubes and nanoparticles such as nanooonions. Therefore, in the $C_{60}$ extract curve, the peak of 560 °C correctly corresponds to $C_{60}$ content. Additionally, the peak at 670 °C might
be related to the presence of nanoonion particles as it will be shown later in the soot analysis by electronic microscopy.

On the other hand, carbon black powder (BP 3700) displays two temperatures of the weight loss at 760 and 840 °C. Pang et al., also found that graphite presents a burning temperature of about 645 °C, at heating rate of 1 °C/min. This last result contrasts with that found by Zhang et al. (1997) for the combustion of graphite. Zhang reported a burning temperature for graphite about 900 °C, at of 20 °C/min. Taking into account that an increase of heating rate causes the burning temperature to increase (Saxby et al., 1992), it is reasonable to speculate that, at 10 °C /min, the burning rate of graphite might be about 800 °C. This finding agrees with the average temperature for the oxidation of carbon black (BP 3700). Here, it is speculated that the two temperatures may be due to the presence of different graphitization degrees into the powder.

Nickel powder shows a decreasing in the DTG curve due to the increase of the sample weight. This increase might be attributed to the formation of some nickel oxides at the beginning of the oxidation reaction.

Figure 6.10 depicts the TG, DTG and DTG Lorentzian fits of the soot obtained in test CB08.

TG curve shows a slightly increase in the weight of the sample before the main combustion. According to Saxby et al., (1992) and Pang et al., (1993), this weight increase is due to addition of oxygen atoms to the carbon structure. These authors have reported a similar chimisorption effect in fullerenic soot containing a mixture of various forms of carbon. Once combustion has commenced, loss of carbon proceeds smoothly to completion. The initial burning temperature of the raw-soot is about 300 °C. Five stepwise weight-loss can be also identified in the DTG curve. According with the analysis presented above, the first peak at 430 °C might be assigned to small particles of amorphous carbon, the second at 510 °C to fullerenes, third at 650 °C any fullerenic structure between C_{60} and nanoonions, the fourth at 715 °C to nanotubes/nanoparticles and the last at 800 °C to graphitic structures. (See also Figure 6.9). It must be admitted that the relative allocations of the peaks have been performed accepting that any peak displacement can happen due to the differences in the heating rate used in this work and references.
The results also show that the resistance to oxidation depends on the carbon network of the graphitic structures. For example, the conformational strain of the C_{60}/C_{70} molecules is overall higher than that nanoparticles (nanoonions) and nanotubes, which in turns is higher than that of graphite. Thus, graphite demands higher activation energy for oxidation because its planar surface in which aromatic bonding dominates and dangling bonds are minimal. In contrast, the presence of pentagons in nanotubes, nanoonions and fullerenes produces curvature and increased strain. These areas might be considered as likely initial sites in which oxidation reactions finally occur.

Although TGA is considered as a useful analytic technique to quantify the concentration of structures, here, the quantitative results obtained with this technique are considered doubtful due to the overlapping of curves. For example, the relative surface area for the fullerene peak at 510 °C is estimated to be about 30% of the total mass of raw soot. This result defers from
that obtained by UV spectrophotometry for C_{60} content. It is thought that a further purification procedure is mandatory in order to better separate carbon structures before analysis.

However, from the results it is evident that various graphitic structures are produced during the synthesis of fullerenes.

6.4.2 Scanning Electron Microscopy

In order to evaluate the carbon nanostructure morphology, scanning electron microscopy analyses were performed.

Just like Figure 6.2, two *encapsulate* unreacted particles are shown in Figures 6.11 and 6.12. These pictures confirm the results of particle vaporization found in Chapter 5. Because the large size of the particle agglomerates of the starting mixture, particle vaporization is not always completely achieved. Particle vaporization plays an important role in the gaseous carbon concentration inside the reactor and fullerene growth.

![SEM Image of an Unreacted Particle Surrounded by Carbon Layers](image)

Figure 6.11 SEM Image of an Unreacted Particle Surrounded by Carbon Layers
According to micrographs, it is speculated that graphitic layers may cover catalyst particles. These layers might be formed through the migration of small carbon species via thermo and photophoresis mechanisms.

Figure 6.12  SEM Image of an Unreacted Particle Surrounded by Carbon Layers and Nanofibers

Carbon nanoparticles produced in the plasma tail are subjected to electric fields, large temperature gradients, and asymmetric absorption of incident radiation within the particle. Electric fields in plasmas cause the charging of nanoparticles enhancing migration and coulomb interactions between ions or electrons and the charged particle. For example, in a conventional D.C. arc discharge process, some of the evaporated material runs directly onto the cathode surface as reported by Ando et al., 2000, and Huczko et al., 2000. In both studies, MWCNTs were formed inside of cathode deposit. Because the high-temperature environment (plasma = 5000 K; cathode surface > 3200 K), high concentrations of C$_2^+$ species and electrical field found in arc plasmas, electrical migration of carbon species may favour cathode deposit and nanofiber/nanotubes growth. In our case, the plasma electrical field may charge electrically non-evaporated micron-sized particles increasing the carbon nanoparticles migration and deposition on its surface.
Thermophoresis is also expected to be present in thermal plasma processes since there always exists large temperature gradients in these systems (Boulos et al. 1994, Chen and Tao, 1992, 1994). Thermophoresis involves the physical phenomenon in which small particles (such as carbon nanoparticles) present in a temperature gradient $\Delta T$ are driven away from regions of higher temperatures. At shown in Table 5.4, plasma temperature is always higher than that of micro-sized particles. These temperature gradients favour ion and carbon atom migration onto the particle surface. Chen and Tao (1992, 1994) performed interesting studies on the thermophoretic force acting on a non-evaporating and evaporating particle under plasma conditions. Their results showed that the thermophoretic force on an evaporating particle might be much greater than that of a non-evaporating. Thus, thermophoretic force may be also enhanced during the evaporation process of the carbon particles. The authors also claimed that ions and electrons cause thermophoretic force at high plasma temperatures, while atoms are mainly responsible at low plasma temperature (less than 7000 K for argon). This allows speculating that, carbon layer may be formed via $\text{C}_2^+$ migration and deposition at the high plasma temperatures observed into the plasma tail. In contrast, at low plasma temperatures such as those found in the reactor section, neutral C and $\text{C}_2$ species may form carbon layers around the particle.

Photophoresis is in some extent similar to thermophoresis because the particle motion is caused by a temperature gradient in the gas adjacent to the particle. However, the temperature gradient in photophoresis arises from non-uniform absorption of incident radiation within the particle. Taking into account that radiative transport is an important feature of heat transfer in thermal plasmas (Proulx et al. 1985), the driving force for particle photophoresis in these systems can be significant. Rosner et al., (1992) reviewed the heat transfer on the dynamics of small particles in gases. They argue that the ratio of the photophoretic and thermophoretic diffusion factors for highly absorbing particles (such as char particles) increases with particle diameter. For example, a char particle of 20 $\mu$m of radius shows a diffusion factor ratio about 0.12. In their study, gas and particle temperature were about 1800 and 1000 K, respectively. Taking into account the plasma and particle temperature estimated in Chapter 5, radiative flux to the particle surface may be higher than 10 % of the conductive flux. Under such conditions, photophoretic effect might also enhanced the deposition rate of carbon particles during the synthesis of fullerenes.
Thus, electrical field effect, thermophoresis and photophoresis can, in some extent, explain the migration and deposition of carbon species onto non-vaporized particles and reactor surfaces. However, the formation of carbon protuberances around particle remains still unclear.

The presence of the carbon layers surrounding the particle are extremely interesting. These nanofiber structures seem to be formed due to an over-saturation and condensation of carbon species on the carbon layer.

From the formation mechanisms shown in Chapter 2 the question is raised whether carbon nanofibers are formed by the overall catalytic mechanism for carbon fiber formation. From this mechanism, it may be speculated that a combined effect of electrical field, thermo and photophoresis causes the migration, diffusion and absorption of small carbon species onto the catalytic particle surface. Then, decomposition reactions lead to chemisorbed carbon species, which diffuse through the surface active sites and precipitate to form the carbon fiber body. The migration of the remaining carbon species around the particle surface forms the fiber skin component. The nanofiber spaghetti-like configuration around the particle seems to be produced by the chaotic movement of the particle into the plasma tail. The nanofiber diameters, inferred from the SEM images, ranged from 20 to 50 nm.

A high density of large carbon nanoparticles and agglomerates also appear in the figures. In terms of their outer diameters (10 - 40 nm), these nanoparticles might be related to nanometric carbon structures also observed by transmission electron microscopy. C_{60} and small fullerenes were not possible identifying because the low magnifications.
Transmission electron microscopy (TEM) analyses were also performed to evaluate the carbon nanoparticle morphology and structure.

A typical carbon nanostructure cluster is pictured in Figure 7.1. This figure also shows a high density of carbon nanoparticles in some kind of flower-like structure. Although the interesting cluster configuration, its carbon particles do not seem to present a specific structure. However, due to their quite small size, these particles might be related to the amorphous carbon detected at 300 °C in the TGA analysis of the C₆₀ extract.

![Carbon Nanoparticle Cluster](image)

**Figure 7.1** TEM Image of a Carbon Nanoparticle Cluster

Figure 7.2 depicts a representative TEM image of condensable material from test CB08. This figure shows the formation of curved carbon layers and amorphous carbon. Here, it is inferred that these curving layers might indicate the growth of fullerenic structures. Because the
growth of flat graphitic sheets is only performed via hexagons, these curving layers might show the growth of hexagon- and pentagon-containing sheets. The concentration of the fullerenic structures might be related with the unknown TGA peak detected at 650 °C. These curving structures present a larger size than fullerenes but smaller size than nanotubes/nanoonions.

![Amorphous Carbon and Catalyst Particle](image)

Figure 7.2 Representative Fullerenic Soot Recovered from Test CB08

7.1 Carbon Nano-Onions

Figure 7.3 depicts a high density of polyhedral structures. These structures are usually called spheroidal fullerenic nanoparticle (Howard et al. 1999), due to their near-spherical geometry. The surface of this nanoparticles is made up of flat faces bonded by curved junctions. The flat faces are composed of polyaromatic sheets (hexagonal), whereas the curved junctions are locations of pentagonal rings, which are characteristics of fullerenic structures. Polyhedral structures are interpreted to be giant fullerenes (Howard et al. 1999). Their geometry, inferred
by the TEM image of the shell cross section, is considered to be icosahedral, i.e. a polyhedron with 20 faces. Here a hexagonal structure is used to clarify this assumption. The estimated angles are about 110 and 130°.

![Image](image.png)

Figure 7.3 Polyhedral Structures in Test CB09

In contrast, Figure 7.4 and 7.5 show the formation of quasi-spherical onion-like particles. The nanoparticle diameter might be estimated to be from 40 to 80 nm.

In 1992, Ugarte reported the curling and closure of graphitic networks under electron-beam irradiation in a high-resolution electron microscope. These conditions resembled a high temperature regime such as those found in an arc and RF plasma reactors. Later, in 1995, the author claimed that onion-like particles might be generated by the graphitization of a liquid carbon drop. The author supposed that the growth of the graphitic layers begins at the surface and progress toward the center of the drop. Ozawa et al. (2002) also studied the transformation of carbon nanoparticles into nanonions by electron beam irradiation. Microscopic observations revealed that the formation of onion-like structures is by a spiral growth mechanism.
Figure 7.4  Onion-Like Structure in Fullerene Soot from Test CB09

Figure 7.5  Carbon Nanoion in the So-Called Twin Configuration
Because it is not possible to distinguish any spiral growth into the structures showed in Figure 7.4, here, it is supposed that formation mechanism may be similar to that proposed by Ugarte (1995).

Interestingly, Figure 7.5 also shows that one nanoparticle is composed by two nanoonions in a twin-configuration.

7.2 Carbon Nanotube

Figures 7.6 and 7.7 show TEM micrographs of a well-formed carbon nanotube found in the soot produced in test CB08. The inner and outer nanotube diameters were estimated as 7 and 15 nm, respectively. The length was approximately 140 nm. Taking into account the external amorphous carbon layer, the estimated external diameter is about 55 nm, while the diameter of the external graphitic layer is about 18 nm.

![TEM Image of a Carbon Nanotube Surrounded by Amorphous Carbon](image)

Figure 7.6 TEM Image of a Carbon Nanotube Surrounded by Amorphous Carbon
These diameter measurements agree with those of carbon nanotubes produced in typical plasma processes (Laurent et al. 1998). Figure 7.7 shows a higher magnification of the carbon nanotube covered with a small amorphous carbon layer. Three concentric walls can be identified into the nanotube in the so-called multiwall (MWCNT) configuration. This configuration is strongly related with the use of large size catalyst particles during the synthesis process as shown in the bibliographic review (Chapter 2).

The reviewed mechanism suggests that the nanotube formation pathway proceeds according the open-ended mechanism. Here, the first step would involve a complete vaporization of the carbon black particles. At the same time, the catalyst particles would be partially vaporized. In the second step, gaseous carbon would be adsorbed by the particle surface. In the third step, carbon species would dissolve, diffuse and precipitate to form the carbon nanotube wall. In the final step, additional carbon species also would precipitate outside of the nanotube forming the external nanotube walls.

Figure 7.7   TEM Image Showing Different Synthesized Carbon Nanostructures
This mechanism is usually proposed when large particles are used as catalyst. However, in this work, this observation remains still unclear because the lack of carbon nanotubes observed in the TEM images.

Taking into account the various carbon configurations identified in these figures, TGA peaks shown in Figure 6.10 may be interpreted. For example, the first peak at 430 °C can be assigned to a high density of nanoparticles of amorphous carbon that have been found associated to nanoonions and the nanotube. The second peak at 510 °C might be associated to small fullerenes such as C\textsubscript{60} and C\textsubscript{70}, which were detected by UV spectrophotometry. The third peak at 650 °C might be related to any fullerenic structure between C\textsubscript{60} and nanoonions. For example, it might be produced by the combustion of any polyhedral structure with only one or two carbon layers.

The formation of nanotubes and nanoonions might explain the TGA peak at 715 °C. The large surface area of this TGA peak might be related with the high concentration of onion-like structures depicted in microographies rather than nanotubes content.

The last peak at 800 °C might represent combustion of large carbon flat layers or the oxidation of unvaporized carbon black particles.
CONCLUSIONS AND RECOMMENDATIONS

The existence of fullerenes and nanotubes was established in the middle eighties and beginning nineties, respectively. During the last fifteen years, systematic efforts have been devoted to improve their synthesis, purification, characterization and applications.

In this work theoretical and experimental studies were carried out to optimize a thermal plasma method for producing carbon nanostructures such as fullerenes and nanotubes. In this method, an induction plasma torch provided concentrated energy for fullerene precursor species activation.

The thermodynamic study revealed that the fullerene formation temperature ranges from 2250 to 3800 K. The C$_2$ and C$_3$ fullerene precursor species are formed above 2500 K.

Thermodynamic results also showed that, when hydrocarbons are used as raw materials, large chains are completely disintegrated at the plasma temperatures (T > 2500 K). Additionally, high concentrations of atomic hydrogen, small hydrocarbon radicals such as CH, CH$_2$ and C$_2$H, and amorphous carbon were also observed in the temperature range of fullerene formation. Hydrogen was shown to have a negative effect on the fullerene synthesis mechanism. This specie decreases the carbon vapor pressure in the plasma reactor and inhibits fullerene growth.

In contrast, when pure carbon is used as starting material, the formation of fullerene precursors and molecules are favoured. The use of high carbon feed rate and high system pressure enhance fullerene yield.

Pure carbon compounds should be used as raw materials while hydrogen-rich molecules should be avoided. High reactor pressure with temperatures between 2500 and 3500 K should be also maintained for optimal fullerene growth.
A kinetic mechanism was also developed to explain the fullerene growth pathway. The mechanism involved the sequential addition of C₂ and C₃ species. Theses species were found to be fullerene precursors during the thermodynamic study.

In general, the results showed that a high solid carbon feed rate speeds up the system reaction rates and increases fullerene yield.

The kinetic results also showed that at lower temperatures (2000 K), fullerene growth proceeds via C₂ additions. At higher temperatures (3000 K) fullerenes are synthesized not only via C₂ but C₃ additions enhancing the fullerene yield.

Although high temperatures and solid carbon feed rates enhance the fullerene yield, these conditions also favour amorphous carbon formation. These results agree with thermodynamic calculations, which show that C₂ and C₃ are in chemical equilibrium.

As expected, preliminary experimental results showed that the use of hydrocarbons as a starting material inhibits fullerene growth. Using C₂H₂ no C₆₀ concentration was found in the soot product. C₂H₂ treatment at plasma temperatures favoured the formation of amorphous carbon, small hydrocarbon compounds and radicals.

C₆₀ was formed when carbon black (CB) and C₂Cl₄ were used as starting material. C₆₀ yields of about 3.6, 2.1 and 3.9 %wt were synthesized when mixtures of CB-Fe and CB-Ni and C₂Cl₄ were used as raw material. HPLC analyses also confirmed the synthesis of C₆₀ as well as C₇₀ fullerene. These results agreed with thermodynamic and kinetic studies showing that pure-carbon compounds promote carbon cluster growth, which enhances fullerene yield.

C₂Cl₄ test showed higher C₇₀ concentration along with other chlororganic compounds. This suggests a fullerene growth process analogous to polycyclic aromatic compounds.

The results of the statistical experimental design indicated that the reactor pressure, plate power and carbon feed rate are the operating parameters that most strongly influence the C₆₀ synthesis. The optimal operating conditions were estimate as: reactor pressure of 66 kPa, plate power of 40 kW and solid carbon feed rate of 2 g/min. The residence time of the carbon gaseous species in the zone of fullerene formation (2250 – 3800 K) was estimated to be about 3 ms.
A low carbon feed rate seemed to enhance the fullerene yield. This experimental result is in contradiction with theory where higher fullerene yields are expected at higher carbon feed rates. The experimentally low fullerene yield was related to poor particle vaporization at higher feed rates. The particle size of carbon-catalyst agglomerates was estimated to be about 115 +/- 57 μm. Computations showed that, at 40-kW of plate power, helium and argon plasma are only able to completely vaporize carbon agglomerate sizes smaller than 100 μm. Thus, larger vaporization times (τ > 3.3 ms) are needed to vaporize larger agglomerates.

This phenomenon was also observed by SEM analyses in which unreacted catalyst particles were found mixed into the soot. SEM micrographs also revealed the presence of some spaghetti-like carbon nanofibers. These fibers were formed around catalyst particles along with a high density of carbon nanoparticles. Further TEM analyses showed not only fullerene synthesis but also graphitic nanoparticles such as onion-like nanostructures and even one multiwall carbon nanotube.

Nevertheless the results presented here provide a sound basis for fullerene and carbon nanostructure formation. Future investigations are suggested for further improvement of the RF plasma system.

A modification of the plasma reactor should be implemented for enhancing yield of fullerenes and nanoparticles. Special attention should be given to the design of the reaction section to improve carbon species annealing at high temperatures and the quenching section to favour carbon condensation. The vaporization process could be improved using different nano-sized catalysts and gas or liquid carbonaceous starting materials. Other operating variables could be studied such as the position of the feed probe and the use of different plasma gases.

A progressive study on the gas carbon species-catalyst interaction should be undertaken. A better knowledge of the carbon reactions on the particle surfaces would contribute to establish scientific basis for the formation mechanism of fullerenes and nanoparticles.

A complete longwise spectroscopic study of the plasma jet should be performed to better understand the role of the C₂ species in the fullerene formation mechanism. Additional characterization techniques will be needed to analyze the morphology and structure of carbon nanoparticles. Raman spectroscopy, high-resolution transmission electron microscopy, and
scanning probe microscopy could be used to study fullerenes, nanoonions and nanotubes at the nanometric and atomic level.

Although many additional efforts should be conducted to better understand the formation of carbon nanostructures, it is evident that the RF plasma reactor approach is one of the most promising technologies for the continuous production of carbon nanostructures in the future.
<table>
<thead>
<tr>
<th>ATTACHMENT 1</th>
<th>LIST OF CHEMICAL COMPOUNDS USED IN THE ACETYLENE THERMODYNAMIC EQUILIBRIUM</th>
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# Attachment 2

## List of Chemical Compounds Used in the Solid Carbon Thermodynamic Equilibrium

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</table>
NOTATIONS

Latin Symbols

$A, B$  Coefficient of the Saturated Vapor Pressure Equation
$a_i, ..., a_7$  Coefficients of the Fitting Equations $C_p, H^o, S^o, U^o$ and $G^o$
$A_i$  Pre-exponential Factor for the $i^{th}$ Reaction
$a_{ki}$  Gram-Atom Number for the $k^{th}$ Element in a Mole of the $i^{th}$ Gaseous Specie
$A_o$  Pre-exponential Factor
$A_p$  Surface Particle Area ($m^2$)
$Bi$  Biot Number
$C_n$  Fullerene Molecule
$C_p$  Molar Heat Capacity ($J/mol \, K$)
$d$  Carbon Nanotube Diameter ($\mu m$)
$d_p$  Particle Diameter ($m$)
$E$  Activation Energy ($kJ/mol$)
$E_{J}, E_{J^*}$  Rotational Levels in the Upper and Ground Triplet Electronic States
$f_i$  Partial Fugacity of the $i^{th}$ Gaseous Specie
$f_i^o$  Fugacity of the $i^{th}$ Gaseous Specie at the Reference State
$f_{nm}$  Electronic Oscillator Strength for $C_2(d-a)$ Transition
$f_o$  Vaporized Fraction of the Particle
$G_c$  Carbon Mass Flow Rate ($kg/s$)
$G_g$  Forming Gas Mass Flow Rate ($kg/s$)
$G_i^o$  Gibbs Free Energy of the $i^{th}$ Gaseous Specie
$G_j^o$  Gibbs Free Energy of the $j^{th}$ Condensed Specie
$G_{mix}$  Gibbs Energy of the Mixture ($kJ/mol$)
$G^o$  Molar Gibbs Energy ($J/mol$)
$G'$  Total Gibbs Energy of the Reacting System ($kJ/mol$)
$h_c$  Heat Transfer Coefficient ($J/m^2 \, s \, K$)
$H_{cg}$  Gas Carbon Enthalpy ($kJ/kg$)
$h_{cs}$  Solid carbon Enthalpy ($kJ/kg$)
\( H_g \)  
Forming Gas Enthalpy (kJ/kg)

\( H' \)  
Molar Enthalpy (J/mol)

\( H_p \)  
Specific Plasma Enthalpy (kJ/kg)

\( H_s \)  
Latent Heat of Sublimation (J/kg)

\( J_{\text{exp}}, J_{\text{calc}} \)  
Characteristic Peaks in the Rotational Structure for the Experimental and Simulated Spectra

\( J'(J'') \)  
Rotational Quantum Number of the Total angular Momentum

\( K \)  
Constant of vaporization rate (s\(^{-1}\))

\( k^- \)  
Plasma Gas Thermal Conductivity (J/m s K)

\( K_c \)  
Equilibrium Constant

\( k_f, k_r \)  
Forward and Reverse Rate Constant

\( k_p \)  
Particle Thermal Conductivity (J/m s K)

\( m \)  
Number of Hexagons in a Fullerene Molecule

\( m_p \)  
Mass of the Carbon Particle (kg)

\( n \)  
Number of Carbon Atoms in a Fullerene Molecule

\( n_i \)  
Mole Number of the \( i \)\(^{th} \) Gaseous Specie

\( n_j \)  
Mole Number of the \( j \)\(^{th} \) Condensed Specie

\( N_{mv-L} \)  
Column Density of \( C_2(a^3\Pi_u, v''=0) \)

\( Nu \)  
Nusselt Number

\( P \)  
Plate Power (kW)

\( p \)  
Pressure (kPa)

\( q_{vv'} \)  
Franck-Condon Factor

\( Q \)  
Net Heat Exchange Between Particles and Its Surroundings

\( Q'_{r}, Q''_{r} \)  
Rotational Statistical Sums for d\(^3\)\( \Pi_g \) and a\(^3\)\( \Pi_u \)

\( R \)  
Chiral Vector

\( R \)  
Gas Constant (8.314 kJ/mol K)

\( S_{J,J'} \)  
Hou-London Factor

\( S^o \)  
Molar Entropy (J/mol K\(^2\))

\( T \)  
Temperature, Plasma Temperature (K)

\( t \)  
Time (s)

\( t_r \)  
Residence Time (s)
$T_a$  
Surrounding Temperature (K)

$T_e$  
Electron Temperature (K)

$T_h$  
Heavy Particle Temperature (K)

$T_P$  
Particle Temperature (K)

$U^o$  
Molar Internal Energy (J/mol)

$V$  
Average Velocity Between Two Points in the Plasma Tail (m/s)

$X_k$  
Chemical Symbol of the $k^{th}$ Specie

$[X]$  
Molar Concentration (mol/cm$^3$)

$Z_1, Z_2$  
Axial Distance of Two Consecutive Points in the Plasma Tail (m)

**Greek Symbols**

$\Delta G_i^o$  
Standard Gibbs Energy (kJ/mol)

$\Delta H_e^o$  
Standard Combustion Enthalpy (kJ/mol)

$\Delta H_f^o$  
Standard Formation Enthalpy (kJ/mol)

$\Delta H_{sub}^o$  
Standard Sublimation Enthalpy (kJ/mol)

$\Delta H_{tr}^o$  
Standard Transition Enthalpy (kJ/mol)

$\beta$  
Temperature Exponent

$\varepsilon$  
Particle Emmisivity

$\varepsilon_{ij}(V)$  
Spectral Line Emission Coefficient

$\kappa(V)$  
Spectral Line Absorption Coefficient

$\nu$  
Wavenumber

$\nu', \nu''$  
Forward and Reverse Stoichiometric Coefficient

$\theta$  
Chiral Angle (°)

$\rho_p$  
Particle Density (kg/m$^3$)

$\sigma_s$  
Stefan-Boltzmann Constant ($5.67 \times 10^{-8}$ J/s m$^2$ K$^4$)

$\tau$  
Time for a Complete Particle Vaporization (s)
REFERENCES


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CRTT, (2002). Research Center in Plasma Technology, Thermal Plasma Laboratory, Universite de Sherbrooke, Canada.


DIKY, V. V., KABO, G. J. (2000). Thermodynamic Properties of C_{60} and C_{70} Fullerences, Russian Chemical Reviews, vol. 69, n. 2, p. 95-104.


