PRODUCTION OF CARBON NANOSTRUCTURES USING A HF PLASMA TORCH
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Abstract
Carbon nanostructures (CNSs) (fullerenes and nanotubes) have been produced using an
effective H. F. induction plasma reactor. Both, acetylene and carbon black (CB) were used as
source of raw materials and different metallic powders as catalysts. Thermodynamic
equilibrium computations demonstrate that active species of C₂ and C₃ play an important role
in the mechanism of nanostructures formation. Further, a series of experiments were carried
out to evaluate the effect of the feed rate of raw material and the influence of different
catalysts on the synthesis of carbon nanostructures. Our preliminary experimental results
indicate that the presence of hydrogen in the reactor environment inhibits the production of
CNSs whereas the evaporation of a CB-Fe mixture produced a concentration of 3.6 wt% of
C₆₀ in the soot collected in the reactor.

1. Introduction.
The discovery of fullerenes by Kroto and coworkers in 1985 [1] and carbon nanotubes
(CNTs) by Endo in 1988 [2] have been important contributions that marked the development
of new methods involved in the synthesis and production of carbon nanostructures (CNSs).
As a result, the last decade has experienced increased research interests in the manufacture of
CNSs, and several systematic efforts to improve their synthesis have been proposed [3, 4, 5].
Nowadays, CNTs are of particular interest because they exhibit several distinctive properties
with a wide range of technological uses. The applications of CNTs are various and include: 1)
the use of their field-emitting properties to produce electronic displays, 2) the utilization of
open-ended CNTs as ultra-small pipettes to inject molecules at the cellular levels, 3) the use
of nanoprobes in scanning-probe microscopy techniques, and more recently, 4) CNTs
products are being used as hydrogen storage device in the application of fuel cells.
In this study we propose a new method to produce CNSs. Our method is based on the
evaporation of carbon and catalyst particles using a H. F. induction plasma torch as source of
energy to activate the precursor species. Some of the most significant chemical and physical
phenomena involved in the method’s ability to more efficiently synthesize the 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
temperatures, residence times, species density, and species transport throughout the different
temperature gradients.
In addition, in our method, the H.F. plasma system has the ability to control independently 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. In the experiments illustrated below, a mixture of acetylene-catalyst and carbon black-catalyst was used as source of raw materials. The electrical power of the plasma torch and the reactor pressure were constant and maintained at 40 kW and 66 kPa respectively. The yield of CNSs was determined by UV spectrometry and their morphological characterization was made using scanning electron microscopy (SEM). The results indicate that the presence of hydrogen in the reactor’s atmosphere strongly affects the CNSs formation. Also, the CNSs yield was higher when carbon black-iron mixture was used as starting material.

2. Thermodynamic Considerations.
According to one of the most important mechanisms developed to explain the fullerene formation (6), the evolution of carbon atoms is through the following path: from atoms to molecules to chains to two-three-ring system to fullerenes. In this mechanism, the transitional stage from three-ring system to fullerenes is strongly affected by the concentrations of C₂ and C₃ species.

The thermodynamic calculations have provided significant information regarding the equilibrium composition of these species in a reaction system. Using the computer software FACT-WIN version 3.05, a thermodynamic analysis was performed to predict the concentration of C₂ and C₃ species as a function of the temperature. The computation model is based on the minimization of the Gibbs free energy, which considers that the total free energy of a reaction system is minimum when the thermodynamic equilibrium is reached. Figure 1 shows the equilibrium composition as temperature function, of the system C₂H₂:Fe:He:Ar. The initial concentrations of the system’s reactants were 0.03:0.3:135:28 mol, respectively. Also, 15 gaseous and three solid species (right column of Fig. 1) were considered in the study at a pressure of 100 kPa.

![Thermodynamic Equilibrium for the System C₂H₂:Fe:He:Ar-0.03:0.3:135:28 mol at 100kPa.](image)

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. According to Chang (7), the most representative temperatures in a plasma system are
considered above the 2500 K, and due to this, it is quite likely that the formation of fullerene will be favored in the plasma system.

3. Experimental.
Two different test series were performed during the experimental part of this study. In the first testing series, the sources of raw material were mixtures of acetylene-iron and acetylene-nickel-cobalt (99.8%, -325 mesh), whereas in the second series the raw material included mixtures of carbon black BP 3700-iron. In both experiments, the reactant mixtures were introduced axially through a water-cooled probe.

All the experimental tests were carried out according to the experimental setup shown in Figure 2. A Tekna PL-50 plasma torch with a quartz confinement tube of 50-mm i.d. and 4-turn coil was used to vaporize the mixtures of reactants. The plasma gas flow rates applied were as follow: central gas 30 slpm (Ar), sheath gas 120 slpm (He) and powder gas 8 slpm (He). The RF power supply was a Lepel 60 kW unit with an oscillator frequency of 2 to 5 MHz.

![Figure 2. Experimental Setup of the Carbon Nanostructures Production Process Showing the Different Components Involved in the System.](image)

While the experimental design was considered as a single model unit, the equipment used was separated in two sections for practical and technical purposes. One section included the reactor (150-mm i.d., 500-mm long) and the quenching zone (130-mm i.d., 500-mm long). The other section included the filtration system, which in turn comprises a cyclone and two stainless steel filters (38-mm o.d., 350-mm long). Both sections had a water-cooled jacket which function was to condense the carbon vapor before exhausting the gas to the vacuum pump.

The energy efficiency of the torch and that of the overall system was computed assuming that the heat losses of the system are only due to the cooling water circuits. To estimate these efficiencies, the following equations were used:
Torch efficiency \( \eta_t = \left[ 1 - \frac{H_{wp} + H_{wt}}{U_p I_p} \right] \times 100 \)

Overall efficiency \( \eta_o = \left[ 1 - \frac{H_{wp} + H_{wt} + H_{so} + H_{st}}{U_p I_p} \right] \times 100 \)

Where \( H_{wp}, H_{wt}, H_{so}, \) and \( H_{st} \) are the heat losses due to the probe, torch, reactor and filters, respectively. \( U_p \) and \( I_p \) are the plate voltage and current of the power supply.

The soot was collected at the bottom of the quenching section, the filters and the cyclone. The morphological and structural characterization of the nanoparticles produced during the experiment was analyzed with the aid of a Scanning Electron Microscope (SEM) LEO 1530. A UV absorption spectrometer (at 329 nm) was used to quantify the yield of fullerenes during the experimental part.

4. Results and Discussion.

Both types of parameters, constant and variable were considered in this study. The operating conditions used during the experiments are summarized in Table 1. The variable parameters included were the source of raw materials (acetylene and carbon black), the type of catalyst (Fe, Co-Ni), and the raw material-catalyst ratio. Among the constant parameters included were the powder, central, and sheath gas flow rates, the reactor pressure and the electrical power, their values are also indicated in Table 1 along with the specific running time for each test.

<table>
<thead>
<tr>
<th>Test No</th>
<th>Catalyst</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>0.4 slpm (C(_2)H(_2))</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>1.5 (Co-Ni)</td>
<td>1.5 slpm (C(_2)H(_2))</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>1.2 (Fe)</td>
<td>8.0 slpm (C(_2)H(_2))</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1.5 (Co-Ni)</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>1.4 (Co-Ni)</td>
<td>2.0 slpm (C(_2)H(_2))</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>1.5 (Co-Ni)</td>
<td>8.0 slpm (C(_2)H(_2))</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>0.24 (Fe)</td>
<td>0.3 g/min (CB 3700)</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>0.9 g/min (CB 3700)</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>0.52 (Fe)</td>
<td>1.3 g/min (CB 3700)</td>
<td>15</td>
</tr>
</tbody>
</table>

The energy efficiency of the torch was estimated as 74% and the estimated value of the overall efficiency was 30%. In order to evaluate the effect of the plasma on the catalyst
structure, tests one and four were carried out without feeding raw material into the system. The effect of these changes was an increase in the catalyst's specific surface area after the plasma treatment. Normally, iron passed from 0.9 to 16.2 m$^2$/g whereas nickel passed from 0.6 to 15.1 m$^2$/g. Nonetheless, these results indicate a decrease in the particles size of the catalyst. Further, no elongated nanostructures were observed with the SEM.

On the other hand, a very light soot-like product was found deposited in the reactor walls, in all the tests of carbon vaporization performed. When acetylene was used as raw material, flying threads of soot falling down into the reactor were observed. The plasma color also varied during the experiments, and the color depended on the type of catalyst used. For instance, when Fe and the Co-Ni mixture were used, green and blue colors were respectively observed.

In Table 2 the mass balance for each test, defined as percent of the recovered mass (total recovered mass X100/total feeding mass) is summarized along with the most significant results in terms of C$_{60}$ contents. The differences of the 100% in the mass balance can be explained based on the fact that a portion of the soot rested attached to the walls of the experimental equipment and another part was released to the environment during the soot recovering process.

The results show that C$_{60}$ was preferably formed under the presence of iron. This finding is likely correlated with the specific surface and the body centered cubic structure of the iron. The iron's specific surface and crystalline structure are relevant aspects during the catalytic process because they are involved in the contact and the reaction sensitivity between the catalyst and the reactants. Figures 3 and 4 show SEM micrographs of an unreacted particle covered with some spaghetti-like nanostructures. This particle survived the plasma conditions without evaporation. In terms of the outer diameter (20-30 nm), the nanostructures in the particle can be considered as carbon nanotubes (8). Also, a high density of carbon shells were found associated to the nanotubes: the diameters of these carbon shells ranged from 10 to 50 nm. Additionally, graphite layers are surrounding the metal particle of iron in the so-called "encapsulate" configuration.

<table>
<thead>
<tr>
<th>Test N.</th>
<th>Recovered Mass (%)</th>
<th>Fullerene Content (% wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.8</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>84.6</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>63.2</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>99.7</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>78.1</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>67.3</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>80.2</td>
<td>3.9</td>
</tr>
<tr>
<td>8</td>
<td>44.4</td>
<td>1.0</td>
</tr>
<tr>
<td>9</td>
<td>92.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The high yield of carbon nanoparticles and the lack of carbon nanotubes seem to be associated to two main factors. The first one is related to the size of the catalyst particle used (>5 μm) in the experiment. When large catalyst particles (>20 nm) are used, carbon nanofibres and nanoparticles are formed, conversely, the use of small catalyst particles (<20 nm) favors the yield of carbon nanotubes (8). The second factor is 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 is five times lower than that of 3.0 mg/s/kW used in the conventional arc plasma processes (9) proposed in previous studies.

5. Conclusions.
This study demonstrates the potential use of an H.F. induction plasma system for the production of carbon nanostructures using acetylene and carbon black as sources of raw material and basically, Fe as catalyst. The thermodynamic analysis indicates that within the temperature range that characterizes the plasma, the concentration of C, and C, species is considerably higher. These concentrations favor the formation of fullerenes. Our results reveal that the higher yield of fullerenes is produced when carbon black-Fe mixtures are fed to the plasma system. It appears that relatively higher yield of fullerenes is obtained with the operating conditions used in our experimental design. However, in order to improve the yield of carbon nanotubes, the use of metal catalyst particles in the nanometer size range (<20 nm) and a higher vapor pressure of the carbon feeding to the reactor must be considered. Overall, the preliminary results presented here provide a sound basis for further investigation towards the improvement of plasma systems to produce carbon nanostructures. It is evident that H.F. plasma approaches emerge as one of the most promising technologies to produce higher volumes of carbon nanostructures in the future.

6. References.