PRODUCTION OF CARBON BLACK USING INDUCTION PLASMA TECHNOLOGY
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1. Abstract.
The research outlined here includes a study of the production of carbon black (CB) in an inductive plasma reactor using dodecane (C_{12}H_{20}) as starting material. The dominant species prevailing in the equilibrium of the operating conditions were evaluated based on the thermodynamic studies of the Ar-C-H and Ar-C-He systems. Likewise, and in order to determine in which portions of the plasma torch the optimal degradation conditions are found, we conducted a hydrodynamic characterization of the liquid atomizer. The influence of the different operational conditions in the reactor, such as the feed rate of dodecane, the reactor pressure, the plate power applied on the plasma torch, and the composition of plasma gas in the production of carbon black is discussed along with relevant results obtained when He was used as sheath gas; the carbon black produced was of high purity and had remarkable properties. Finally, the thermal efficiency of the process was also estimated.

2. Introduction.
The term "carbon black" refers to a group of industrial products involving thermal, furnace, channel, and acetylene black. They essentially consist of elemental carbon in the form of nearly spherical particles of colloidal size, coalesced into aggregates and agglomerates. Carbon black plays an important role not only as a reinforcing filler for tires and other rubber goods but also as a pigment for printing inks, coatings, plastics and a variety of applications in our daily life.

At present, the total world production of Carbon Black is about 6 million tons per year (1) and most of its industrial production is based on the process involving the "incomplete combustion" of hydrocarbons (in which the "Furnace process" is the main one). Some of the characteristics of the "Furnace process" include poor carbon yield, and low value and high pollution levels of off-gases (CO_2, NO_x, VOC, SO_2, etc.), and one of its greatest advantages implies the loss of hydrogen as valuable by-product during the process.

Because of the temperature range (2500 to 10 000 K) that facilitate the formation of numerous radical species, thermal plasma processes are considered among the most promising technologies to produce a large gamma of carbon black with special properties (1, 2, 3). In addition to enabling the production of this special carbon black, this technology also improves the energetic efficiency of the reaction and reduces the emission of contaminants due to the complete decomposition of the feed raw material.

The purpose of this investigation is to study the effect of different operating conditions in the synthesis of carbon black in an inductive plasma reactor using dodecane (C_{12}H_{20}) as starting material. The use of an inductive plasma torch for treatment of liquids offers many advantages: for example, it provides the means for simple injection of liquid as well as larger specific plasma volumes of lower plasma gas velocities, which in turn allow for a better control of the process’ chemistry. In this study, special emphasis is made on the
characterization of the liquid atomizer in order to select the parameters at which the smallest
diameter of the drop is found during the injection of the dodecane.

3. Thermodynamic Study.
The composition of the thermodynamic equilibrium for the $C_{12}H_{26}$-Ar-He and $C_{12}H_{26}$-Ar-H$_2$
systems was computed using the computer program FACT-Win Software version 3.05
(Thermfact/CRCT). This program is based on the method of Gibbs free energy minimization
and has the following assumptions: 1) that the gases are ideal and thus form ideal mixtures,
and 2) that condensed species are not miscible. In our study, a total of one hundred and thirty-
two species obtained from Fact-Win Databank were considered. The initial conditions used in
the two systems were the following. In system one we considered $C_{12}H_{26}$-Ar-He:0.0145-
1.0225-5.194 mol, and for the system two the conditions were $C_{12}H_{26}$-Ar-H$_2$:0.0145-4.7033-
0.04089 mol. The atomic C/H ratios for the reaction systems were 0.46 and 0.14, respectively.
The studies were conducted at temperature ranges that varied from 500-4000 K at atmospheric
pressure.

![Figure 1. Equilibrium Composition for the System $C_{12}H_{26}$-Ar-He with $C_{10}$ at 1 atm](image-url)

Figure 1 shows the equilibrium composition of the system investigated as a function of the
temperature. When the temperature is lower than 1000 K, a higher concentration of
hydrocarbon saturated molecules like $CH_4$, $C_3H_6$, and $C_4H_8$, are present (Fig. 1). Also,
concentrations of solid carbon, hydrogen, acetylene and unsaturated radical species are most
commonly found between 1200 and 3000 K, and the presence of atomic species like $H_{2g}$, $C_{1g}$,
$C_{2g}$ become important at higher temperatures.

The co-existence of two different equilibrium regions in the overall degradation process of a
hydrocarbon by plasma process has been discussed by Soncya (4), in which he explains the
presence of polycyclic aromatic hydrocarbons (PAH) and benzene. These two regions are
evident in the thermodynamic study shown here. The first region is located directly in the
plasma (where solid carbon participates in the equilibrium up to 3500 K, as indicated
previously). However, if the full equilibrium state is not reached in the gas phase, a second
region called "the pseudo-equilibrium state" may be observed due to kinetic limitations and
the solid carbon deposited on the wall. To predict this pseudo-equilibrium, a new computation
analysis was made, this time considering the system without $C_{10}$. With these changes, the
production of benzene ($C_6H_6$) and PAH as naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$) become also important up to 1000 K.

When the objective is to produce a high yield of solid carbon, an important consideration is the atomic C/H ratio in the feed stream. Thus, when H is fed as reactant, the yield of solid product decreases. Likewise, the production of aromatic compounds decreases while saturated species are formed. This finding shows agreement with our experimental results.

4. Atomization Study.
In our study we also investigated the influence of the operating conditions of the liquid atomizer on the atomization quality. A "plain-jet" atomizer was selected because of its basic design, features, and its adaptability as feeding probe in plasma reactors. The measurements of the mean drop size (Sauter mean diameter, SMD) formed were obtained using the well-established light-scattering technique. During the experimental part, we used an air-water system to carry out all the tests. The variable parameters were as follows: airflow rate (5, 10, 15, 20 slpm), liquid flow rate (3.3, 9, 14, 21, 24 ml/min), and the axial distances from the nozzle exit were (0, 4, 8, 12, 16, 20, 24, 28 and 32 cm).

![Figure 2. Variation of the Mean Drop Size with the Relative Air Velocity.](image)

Overall, our results confirm those obtained in previous investigations (5). The most important factor that influences the SMD is undoubtedly, the air velocity. In general, SMD values decrease when the relative air velocity increases. The influence of the relative air velocity on SMD for an axial distance of 4 cm from the exit of the nozzle is shown in Figure 2. It is clear that SMD decreases when the air velocity increases for any liquid flow rate used, however, after 900 m/s the SMD becomes constant (Fig. 2). This result highlights the importance of the design in the airblast atomizer to arrange for liquid jet to be exposed to the highest possible air velocity consistent with the available pressure drop. In all the tests, the maximal SMD observed was smaller than 40 μm. On the other hand, this study also demonstrated (figure not included) that the SMD as function of the axial distance from the exit of the nozzle, can be considered constant for the range in which the probe is located into the plasma torch (0 to 6 cm).

Therefore, the optimal operating conditions of the atomizer selected to carry out the experimental tests were: an axial distance of 4 cm (from the exit of the nozzle) and an airflow
rate of 10 slpm. In addition, the liquid flow rate selected was modified as a variable factor during the experimental part.

5. Experimental Procedures.
The experimental setup used in this study includes the major pieces of equipment and the material involved during the procedure (Figure 3). To begin with, dodecane (C\textsubscript{12}H\textsubscript{26}) with a degree of purity of 99% was fed through a plain jet gas-blast atomizer using a peristaltic pump. A plasma torch model Tekna PL-50 model with 50-mm i.d. quartz tube and 4-turn coil was used to dissociate the dodecane molecule. The point of injection was located in the third coil of the torch because this zone corresponds to the region of highest mean plasma temperature and is where the better quality in the atomization takes place. The atomization gas, either in the form of hydrogen or helium was fed at a rate of 10 slpm. The RF power supply was a LEPEL unit of 60 kW with an oscillator frequency of 2 to 5 MHz.

![Figure 3. Experimental Setup of the CB Production.](image)

The equipment used in this experiment was separated in three sections. The first section included a reactor with 150-mm i.d. and 500-mm long. The second section comprised the quenching zone with the following specifications: 130-mm i.d. and 500-mm long. Sections one and two had a water-cooled jacket in order to stop the reaction and begin the condensation of the products. Finally, the third section included a filtration system, which contained three stainless steel filters with 60-mm o.d. and 457-mm long. The gas products were analyzed using the on-line gas chromatograph model GC 3800 Varian equipped with two detectors; the Thermal Conductivity Detector (TCD) for H\textsubscript{2} analysis and the Flame Ionization Detector (FID) for hydrocarbon analysis. The solid products collected separately in the reactor walls and in the filters zone of the reactor were analyzed with the aid of a Scanning Electronic Microscopy (SEM) model LEO 1530. Additional analyses to determine the elemental analysis of the solid products were made using a Leco analyzer.

6. Results and Discussion.
The main findings and operational conditions used in this investigation are summarized in Table 1. The flow rates of plasma gas were different depending on the sheath gas used. That is, when H\textsubscript{2} was used the flow rates values of plasma gas were: central gas (30 slpm Ar),
sheath gas (80 slpm Ar and 10 slpm He) and powder gas 10 slpm (Ar). In contrast, when He was used as sheath gas, the values used were: central gas (30 slpm Ar), sheath gas (120 slpm He), and powder gas (7 slpm He). In addition, our experiments included a 10 minutes stabilization period of the plasma and the feeding of dodecane in order to reach a steady state. This was followed by the on-line chromatography analysis. All the data relevant to the mass and energy balance was recorded for analysis purposes. The energy efficiency of the torch was estimated as 72.2% and the overall efficiency was 41.2%.

Table 1. Operating Conditions of Carbon Black Production

<table>
<thead>
<tr>
<th>Test</th>
<th>Pressure (Torr)</th>
<th>Plate Power (kW)</th>
<th>Feed rate (ml/min)</th>
<th>Sheath Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>40</td>
<td>3.3</td>
<td>He</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>40</td>
<td>3.1</td>
<td>He</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>40</td>
<td>6.6</td>
<td>He</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>20</td>
<td>5.6</td>
<td>Ar - H₂</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>40</td>
<td>4</td>
<td>Ar - H₂</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>40</td>
<td>10</td>
<td>Ar - H₂</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>20</td>
<td>10</td>
<td>Ar - H₂</td>
</tr>
<tr>
<td>8</td>
<td>300</td>
<td>20</td>
<td>4.8</td>
<td>Ar - H₂</td>
</tr>
<tr>
<td>9</td>
<td>500</td>
<td>20</td>
<td>4.3</td>
<td>Ar - H₂</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
<td>20</td>
<td>9</td>
<td>Ar - H₂</td>
</tr>
</tbody>
</table>

Our results indicate that several factors played a significant role in the production of carbon black. Of these, the plasma power, the helium atmosphere, and the reactor pressure appear to be the most important during the experimental part. Also, when He was used as sheath gas and a high system pressure and plasma power were used, a higher percent of carbon black mass was recovered (Figure 4). This means that a higher value of plasma power permitted the entire decomposition of the dodecane molecule, which was subsequently transformed in carbon black. A high carbon black yield was also observed in all the tests performed when He was used in the sheath gas. This high yield is explained because the atomic C/H ratio takes a bigger value in the He-based systems than those systems where H₂ is present (this concept was been previously explained in the thermodynamic study section). At last, the low production of acetylene representing the saturated hydrocarbon was also observed.

Fig. 4. Results of Mass Balance and C₂H₂ Yield.

Fig. 5. SEM Image of the CB Produced with the H.F. Plasma System when He was used in the Sheath Gas.
The effect of the pressure is evident when different tests performed during the experiment are compared. For instance, there is a 200 Torr difference between test 1 (500 torr) and test 2 (300 torr). The increase in the carbon black yield in test 1 relative to test 2 is most likely related to the contraction of the plasma volume when the pressure of the system increases. In general, the residence time of the dodecane decreases when the plasma volume is smaller. Moreover, the cooling effect of the liquid injection into the center of plasma becomes gradually more important.

The increase of the dodecane feed rate shows a strong influence in the plasma due in part to the cooling of the plasma flame; consequently, an incomplete decomposition of the feeding liquid is observed (see values for tests 9 and 10 in Table 1) when a high feed rate of dodecane is used. In addition, all the tests in which the decomposition of dodecane was incomplete, were also accompanied by significant quantities of aromatic compounds (presence of a characteristic odor) and "oil" appearance due to the PAH.

The preliminary results regarding the morphology of the solid product obtained during the experiment are exciting and interesting, particularly when He was used as sheath gas. Our analyses reveal that the product of our experiments corresponds to carbon black, which exhibits a highly organized structure with turbostratic arrangement (Figure 5). This particular structure belongs to the group of thin ramified aggregates, similar to that of acetylene black with average particle size of 10-30 nm. The LECO Elemental analysis reported a highly pure soot (99.69 wt%). No hydrogen (~0.3 wt% of H) was detected. In addition, UV spectrometry (329 nm) revealed the lack of fullerene structures in the soot, thus confirming the high degree of purity of our product.

7. Conclusions.

Our basic procedure involved the production of carbon black via decomposition of C_{12}H_{26} in an induction plasma reactor. The effect of the feed rate of raw material, the reactor pressure, the plasma power and the plasma gas composition on the carbon black production was estimated using a parametric study. The plasma power is one of the most important factors in the experimental yield of the solid product; however the plasma gas composition and system pressure determines the difference in the morphology of the carbon black obtained. Carbon black similar to acetylene black (with interesting properties for conductive applications) was obtained. This product is highly pure. Finally, the phase gas analysis indicates an important production of acetylene (3.3 vol%) when He is present at the sheath gas; this by-product may be considered of high value in this process of degradation of C_{12}H_{26}.

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8. References.