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Continuous Synthesis of Nanocarbons using an Induction Plasma Reactor

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Fullerenes and nanotubes are new forms of carbon nanostructures (CNS's) that have exhibited remarkable properties. The work presented here is focused on the investigation of the synthesis of CNS's using a continuous flow type reactor equipped with an induction (rf) plasma torch. The experimental procedure was based on the vaporization of CB(carbon black)-bearing reactants followed by the condensation of the carbon gas. Thermodynamic studies were performed to predict the equilibrium composition of fullerenes under plasma conditions. An experimental design was used to evaluate the effect of catalyst particles on the fullerene yield. Theoretical and experimental results indicated that iron-carbon mixtures favor CNS formation. C_{60} yields of about 3.9 %wt were synthesized using CB-Fe mixtures while CB-Ni mixtures produced 2.1 %wt of C_{60}. Scanning and transmission microscopy observations revealed that carbon nanofibers, nanoonions and nanotubes were also successfully produced.

Key words: Nanocarbons, Fullerenes, Nanotubes, rf Induction Plasma

1. INTRODUCTION

Historically graphite laser ablation [1] and graphite vaporization using an arc plasma [2] have been the most useful methods utilized for producing carbon nanostructures (CNS's).

During the last sixteen years, several synthesis techniques have been also proposed to improve the yield of fullerenes and nanotubes as reviewed by several authors [3-7]. Among these techniques, rf induction plasma technology has shown to be a good approach to produce a wide spectrum of CNS's. For instance, Peters and Jansen [8, 9] evaporated various solid carbons in a high-frequency (400 Hz) helium plasma batch reactor operated at a power level of 30 kW under a medium pressure. Fullerenes were produced at about 10-18 %wt of C_{60}. Yoshie et al. [10] 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. The fullerene yield was about 7 % when carbon black was used as raw material with a feed rate of 0.5 g/min. Wang et al. [11-13] recently reported the synthesis of fullerenes by direct evaporation of carbon powder (20 μm) using rf thermal plasma at 30-kW power input. According to a spectroscopic study the fullerene yield was related with the intensity of C_2 molecular and C atomic content.

The work presented here is focused on the investigation of the synthesis of carbon nanostructures. The main objectives of this research were to explore the induction plasma technology to in a continuous synthesis of carbon nanostructures, and to predict fullerene formation throughout theoretical studies.

2. THERMODYNAMIC EQUILIBRIUM OF FULLERENES

The equilibrium state of a closed system is described by the total Gibbs energy at a minimum with respect to all possible changes at a given temperature and pressure [14]. Thus, at equilibrium state,

$$\left(dG^t\right)_{T,P} = 0 \qquad (1)$$

In this work, a thermodynamic study was carried out in order to determine the operating conditions in which the formation of fullerene molecules is thermodynamically favored.

The species concentrations of a heterogeneous mixture were calculated by minimizing the total Gibbs free energy of the reacting system at a given temperature. The thermodynamic computations were performed using the computer software FACTSAGE [15] version 5.0.

The reaction system involved the use of carbon black (CB) as starting material and iron (Fe) as catalyst, while argon-helium mixtures were used as a plasma gas.

Thermodynamic data for seventeen gaseous and three solid species were taken into account in the computations of thermodynamic equilibrium. The database involved the more recent thermodynamic data reported for fullerenes.

Fig. 1 shows the chemical equilibrium for the reaction system at total pressure of 101.15 kPa. It can be seen that solid carbon is stable at temperatures lower than 3000 K. The vaporization of solid carbon is reached at temperatures about 3250 K. Iron catalysts is also stable at temperatures lower than 1250 K.

These results suggest that at plasma temperatures (well above 2500 K), all species present in the plasma should be in gas-phase. Therefore, fullerene growth is at best carried out under homogenous reaction conditions.

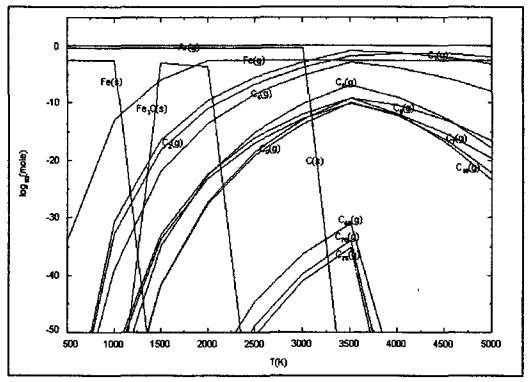


Fig.1 Chemical Equilibrium for the System: 0.4 C + 0.003 Fe + Ar + 5 He, P = 101.15 kPa

As expected, the formation temperature for fullerenes ranges from 2250 to 3800 K. The highest fullerene concentration is reached about 3500 K. This temperature range also corresponds to higher production of precursor species including C_2 and C_3 and small carbon clusters such as C_4, C_5, C_6, C_7, C_8, C_9 and C_{10}. The results also show that the molar mass of carbon clusters decreased with the carbon chain growth. In this way, the equilibrium molar concentration of fullerenes is extremely small and may be considered negligible. This observation suggests that fullerene growth is extremely difficult to achieve when considering only equilibrium plasma thermal effects. Fig. 1 also shows the high stability of iron carbide (Fe_3C) 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.

3. EXPERIMENTAL SET-UP

The experimental tests were carried out according to the experimental set-up shown in Fig. 2.

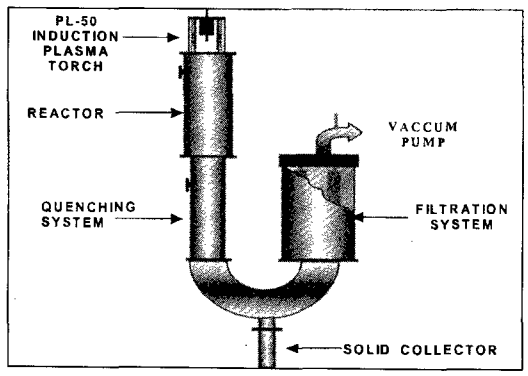


Fig. 2. Experimental Setup for the Production of Carbon Nanostructures.

A Tekna PL-50 plasma torch with a ceramic confinement tube of 50-mm i.d. and 4-turn coil was used to vaporize the mixtures of reactants. The rf power supply was a Lepel 60 kW unit with an oscillator frequency of 2 to 5 MHz.

The experimental equipment 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 comprised three stainless steel filters (60-mm o.d., 457-mm long, rated at 2.8 μm in gas service). Both sections had a water-cooled jacket which function was to condense the carbon vapor before exhausting the gas to the vacuum pump. The reactor and the quenching system included a series of type-K thermocouples to evaluate the temperature zones during the experimentation.

The reactant mixtures were prepared using carbon black powder (BP-3700 or M-280, Cabot Co.) as carbon source and iron (Fe, 98%, 14 +/- 7 μm) and nickel (Ni, 99.8%, <45 μm) powders as catalysts. Only the reactant mixture for test No. 4 was prepared using Fe powder with a smaller particle size (2-4 μm). The reactant mixtures were axially introduced through a water-cooled probe localized at the center of the plasma torch.

After each experiment, the soot was collected from the system and characterized using various analytic techniques. For instance, C_{60} concentration was analyzed using an UV spectrophotometer operated at 329-nm wavelength while HPLC was used to determine the formation of higher fullerenes. In addition scanning and transmission microscopy was used to evaluate the morphology and structure of CNS's.

4. RESULTS AND DISCUSSION

The operating conditions used during the experiments are summarized in Table I. Both types of parameters, constant and variable were considered in this study.

Table I. Operating Conditions Used During Experimentation.

Constant Parameters:	
Powder gas flow rate, Ar:	8 slpm
Central gas flow rate, Ar:	25 slpm
Sheath gas flow rate, He:	120 slpm
Reactor pressure:	66 kPa
Plate power:	40 kW

Test No.	Catalyst Ratio (%mol)	Feed Rate (g/min)	Run Time (min)	Rec. Mass (%)	C_{60} Conc. (% wt)
1	15.0 Fe	0.6	15	***80.0***	***3.6***
2	15.0 Fe	3.4	20	***41.7****	***0.1***
3	8.0 Fe	1.8	15	***91.6***	***0.1***
4	4.0 Fe	2.1	10	***81.4***	***2.2***
5	-	0.7	10	***74.6***	***1.6***
6	2.0 Ni	1.9	16	***85.1***	***2.1***
7	2.0 Ni	4.6	8	***79.6***	***0.3***
8	4.0 Ni	3.7	5	***87.6***	***0.4***
9	4.0 Ni	2.5	7	***90.8***	***0.7***

* Leak in the system

The powder, central, and sheath gas flow rates, the reactor pressure and the plate power were the constant parameters of the process. The variables contained the type of catalyst (Fe and Ni), the raw material-catalyst ratio and the feed rate of the mixture.

Table I also shows the experimental results in terms of the mass balance and the average C_{60} fullerene yields. The differences of the 100% in the mass balance is related to a small leak which was always present during experimentation. In addition, a portion of the soot was lost during the soot collection from the system.

4.1. UV spectroscopic analysis of products

The soot collected from the reactor walls and filter was extracted with toluene using a sonication bath. Toluene extracts of the soot showed a clear purple color characteristic of C_{60} solutions. The extracted solution was analyzed by UV spectrophotometry at 329-nm wavelength.

Surprisingly, the results showed that higher C_{60} concentrations were obtained when catalyst particles were used in the starting material. For instance, it is clear from tests No. 1, 5 and 6 that Fe and Ni played a key role in the formation of fullerenes. Although this catalytic effect of metal particles is not clearly distinguished in these experiments, we speculate that some photocatalytic phenomenon could be produced during the synthesis of CNS's. Indeed, during experiments a stronger plasma radiation was clearly observed throughout the reactor windows. It is well known that metal vapors increase plasma radiation.

Additionally, the results show that C_{60} was mainly formed when a lower powder feeding rate was used. For instance, the highest C_{60} concentration (3.9 %wt) for the CB-Fe mixture was produced using a feeding rate of 0.6-g/min. CB-Ni mixture produced the highest C_{60} yield (2.1 %wt) when a feeding rate of 1.9 g/min was used.

This effect might be explained by a poor vaporization of the raw material particles. When higher feeding rates were used, the plasma temperature decreased due to the high-energy requirements to sublime carbon particles and heat gaseous species. As shown in the thermodynamic study, solid carbon is stable at low temperatures. In addition, low plasma temperatures also favor the formation of small carbon compounds such as C, C_2 and inhibit fullerene formation.

The results also show that the higher C_{60} yields were predominantly produced under the presence of iron. This finding is likely correlated with the smaller particle size of iron as compared with nickel. Therefore, iron was more easily vaporized than nickel. Iron vapors generate a more intense radiation within the plasma, which catalyzes carbon coalescence during the fullerene formation. In addition, metal vapors might also catalyze the growth of elongated carbon nanostructures such as carbon nanofibers and nanotubes as it will be shown later. The iron's specific surface and crystalline structure might be also relevant during the catalytic process of CNS's formation.

Additionally, HPLC analyses were also performed on selected toluene extractions of the soot. HPLC analyses allowed the evaluation of the likely formation of higher fullerenes. The results showed that not only C_{60} fullerene, but also C_{70} was synthesized. The relative C_{70} concentration (C_{70}/C_{60}) produced was estimated to be about 0.08. This experimental ratio contrasts with the equilibrium ratio (0.002) calculated from the thermodynamic study. i.e. 40 times smaller than experimental ratio. It confirms, to some extent, the growth of fullerenes under non-equilibrium thermodynamic conditions.

4.2. Temperature and C_{60} profiles along the reactor axis

In an attempt to evaluate the thermal and kinetic behavior of the plasma reactor, gas temperatures and C_{60} concentrations were determined along the reactor axis. Fig. 3 shows gas temperature and C_{60} profiles for test# 4.

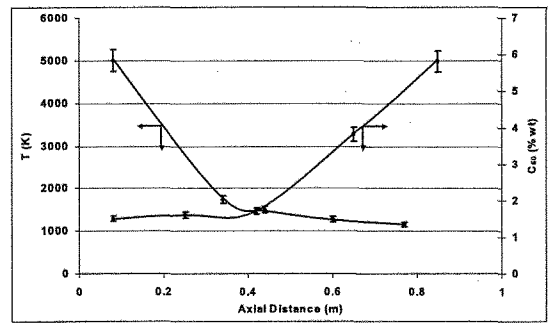


Fig. 3. Temperature and C_{60} Concentration Along the Reactor and Quenching Sections

C_{60} concentrations were determined from samples recovered at different distances along the system.

A first order kinetic equation (2) was used to evaluate the formation of fullerenes

$$\frac{dC_{60}}{dt} = kC \tag{2}$$

where k is the kinetic constant, which was assumed to have an Arrhenius temperature (T) dependence; t is the residence time of the gas, and C and C_{60} are the mass concentration of amorphous carbon and fullerenes, respectively. The residence time of the gas was calculated using an average gas velocity in the reactor of about 1.8 m/s.Direct fitting of experimental data (T, C_{60}/C and t) produced the final value of the kinetic constant

$$k = 0.0732 \exp\left(\frac{444.9}{T}\right) \tag{3}$$

The regression coefficient and the standard error for this equation were estimated to be 0.9625 and 0.0065.

The results of the temperature and C_{60} concentration profiles show that higher C_{60} concentrations are found in the reactor zones at lower temperatures. These results contrast with those found in the thermodynamic study in which fullerenes are formed at high temperatures. This finding can be explained taking into account that the formation-condensation phenomenon of fullerenes occurs continuously along the reactor length. In other words, fullerenes may be formed in the reactor zones at higher temperatures, but they are condensing in the cooler zones following the hydrodynamics of the system.

4.3. Microscopic observations of produced soot

Scanning and transmission electron microscopy analyses were performed to evaluate the carbon nanoparticle morphology and structure.

Overall, the microscopic images showed that carbon nanotubes were preferably synthesized when iron was used as catalyst. Specifically, carbon nanotubes were mainly formed in test No. 4, in which a smaller particle size of catalyst was used. This result confirms the key role of the catalyst sizer during the synthesis of nanotubes.

Fig. 4 shows typical SEM images of the soot recovered at the exit of the plasma torch. A high density

of carbon nanotubes is clearly visible. The produced nanotubes present a wide diameter distribution. Thus, it is thought that the vaporization phenomenon of the starting mixture also plays an important role in the synthesis of nanotubes because an efficient vaporization produces smaller particle size of catalysts and the formation of thin nanotubes might be enhanced.

Interestingly, carbon nanotubes were only found in the soot recovered at the exit of the torch. No nanotubes were found in the soot recovered from the filters. This result suggests that nanotubes are formed in the plasma zones with highest temperature and highest carbon vapor pressure.

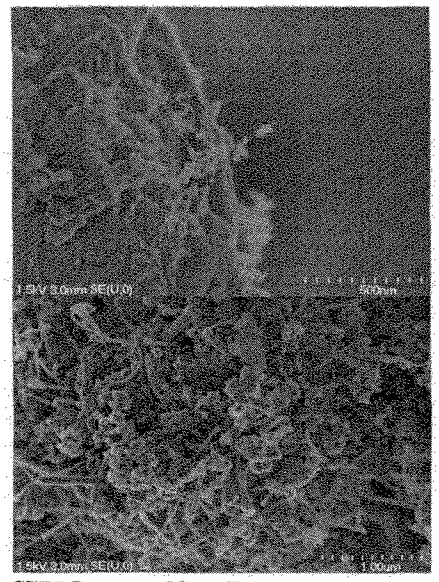
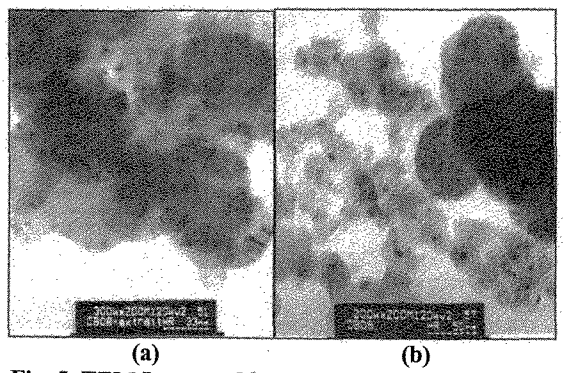


Fig. 4. SEM Images of Soot Recovered from Test #4

Although carbon nanotubes were rarely found in the tests where Ni was used as catalyst, a high density of other carbon nanostructures was also observed.

For instance, Fig. 5 (a) shows a high density of polyhedral structures. These structures are usually called spheroidal fullerenic nanoparticle [16], 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.



(a) (b)

Fig. 5. TEM Images of Soot Recovered from Test #6.

Fig. 5 (b) also shows the formation of quasi-spherical onion-like particles. The nanoparticle diameter might be estimated to be between 40 to 80 nm.

It is here supposed that the formation mechanism of these particles may be similar to that proposed by Ugarte [17, 18]. He reported the curling and closure of graphitic networks under electron-beam irradiation. The author claimed [18] that onion-like particles might be generated by the graphitization of a liquid carbon droplets. The growth of the graphitic layers begins at the surface and progress toward the center of the drop.

5. CONCLUSIONS

Carbon nanostructures (fullerenes, nano-onions and nanotubes) were successfully produced in a rf induction plasma reactor operated in a continuous regime. Thermodynamic and experimental studies showed that nanocarbons are synthesized in the reactor zones at higher temperatures under non-equilibrium conditions. Carbon nanostructures are preferably formed when iron is used as catalyst. In addition, the diameter of carbon nanotubes formed is somehow related with the size of the catalyst particle.

6. ACKNOWLEDGMENTS

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