Continuous Mass Production of Fullerenes and Fullerenic Nanoparticles by 3-Phase AC Plasma Processing

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ABSTRACT

A patented plasma technology has been developed over the last ten years for the continuous mass production of fullerenes and fullerene soot by a French-Belgian consortium. The process combines the high temperature arc method with continuous gas-phase synthesis by injecting solid carbon precursors into a thermal arc plasma. This 3-phase AC plasma process can be considered as a highly flexible process with an enormous potential for further up-scaling to an industrial size at commercially viable cost.

In this paper, the plasma process and results on typical process conditions prevailing are detailed. The main results presented concern the study of the C/He ratio during the fullerene synthesis and its influence on the fullerene yield and on the C_{70}/C_{60} ratio. Price and production short term perspectives for both products are presented.

Keywords: mass production, thermal plasma, fullerene, fullerene soot.

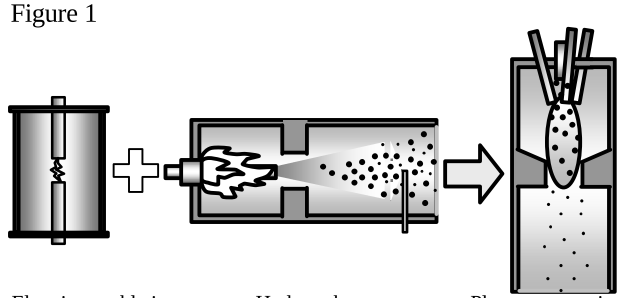
1 INTRODUCTION

For a long time, laser, solar and electric arc processes have been used for fullerene synthesis. Although the fullerene concentration in the soot may be quite high, fullerene production rates remain low, as the material flow is limited to the ablation of a graphite target. For this reason, these processes can hardly be scaleable for industrial exploitation.

In the meantime, the combustion method developed at the Massachusetts Institute of Technology (MIT) by Jack Howard [1] has overcome these problems using an incomplete combustion process. However, the question of greenhouse gas emissions, mainly CO_2, associated with this process may be problematic in the frame of an industrial exploitation. Indeed, only a very small fraction of the hydrocarbon fuel is converted into valuable fullerenes, the remaining fraction being burned and released into the atmosphere [2].

A fundamentally different approach based on a patented plasma technology has been developed over the last ten years by the core partners of a consortium (TIMCAL BELGIUM N.V., EMP-ARMINES and CNRS) [3]. The process combines the high temperature arc method with continuous gas-phase synthesis by injecting solid carbon precursors into a thermal arc plasma (Figure 1).

Figure 1



The plasma technology is totally clean and environmental friendly since zero greenhouse gas emission is produced on site. The success of this approach can be found in the use of a 3-phase AC plasma technology particularly suited for large capacity processing (typically employed in metallurgy).

The possibility to produce large quantities of fullerenes at commercially viable cost will bring their applications to emerge. Especially concerning C_{60}, enormous progresses have been done over the last years in pharmaceutics [4], cosmetics, electronics, etc and industrial users of these molecules are waiting for their abundant availability.

In addition fullerene soot, co-product of the plasma process, is a carbon black-like material that has shown interesting reinforcing properties in rubber and could consequently be of interest for tire and composite industry.

2 PLASMA PROCESS

This 3-phase AC plasma system, initially developed and optimized for the synthesis of novel grades of carbon black [5, 6], has been modified and adapted for the continuous synthesis of fullerenes and fullerene soot [7]. These adaptations lead to the process scheme shown in Figure 2.

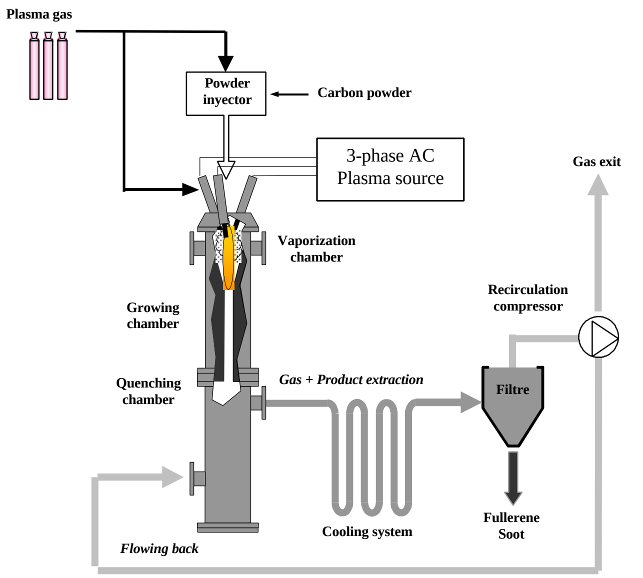


Figure 2: Scheme of the plasma facility configuration for fullerene production

The process can be briefly described as follows: A thermal plasma is generated by an arc discharge between three graphite electrodes placed in the upper part of the reactor. A special powder injection system is employed to mix a solid carbonaceous precursor (powder) with a suspending gas to transport the mixture inside the reactor. This aerosol flows across the arc reaching the high temperature region in the reactor. Due to the high enthalpy density obtained, the solid carbon is vaporized completely while passing through the graphite nozzle. The internal shape of the reactor has been designed to improve the conditions for solid carbon vaporization by a strong confinement of the gas flow. A quenching/sampling system collects the high temperature gas at a predetermined position, cools it down rapidly to the conditions chosen for the production of fullerenes (quenching) and extracts the resulting product from the reactor. The gas is filtered and a part of it is re-injected into the reactor. The fraction that corresponds to the flow rate initially entering the reactor as plasma gas is exhausted. This set-up (with recirculation) allows the extraction of a gas volume superior to the initial flow of plasma gas and therefore disconnects the dependency of these two parameters, which leads to an additional degree of freedom in relation to process operation. Absolute air-tightness of the system is monitored by continuous measurement of the oxygen concentrations at several points of the system.

The plasma process addresses two types of products:

- Fullerenes, mainly C_{60} and C_{70},
- Fullerenic nanostructures based on carbon nanoparticles (carbon-black-like) with particular fullerenic surface structure.

3 PROCESS OPERATING CONDITIONS

A large number of process parameters was investigated. A brief overview is given in Table 1.

Table 1: Main process parameters investigated for fullerene production.

Nature of the carbon precursor	2 carbon black grades 2 acetylene black grades Graphite powder
Nature of plasma gas	Helium Argon Nitrogen
Electric parameters	Arc current, arc voltage
Flow rates	Plasma gas Carbon precursor
Injection conditions	Velocity Location
Quenching and cooling conditions	Velocity (Flow rate) Location of product extraction

The main results presented in this paper concern the study of the C/He ratio during the fullerene synthesis and its influence on the fullerene yield and on the C_{70}/C_{60} ratio. Therefore, the plasma zone has been characterized also by optical emission spectrometry.

4 PROCESS CHARACTERIZATION

- Temperature Measurement by Optical Emission Spectrometry.

As part of the plasma zone characterization during process operation, optical emission spectroscopy was employed. The experiments were performed with helium as plasma gas. During fullerene synthesis, C_2 is produced from carbon particle vaporization as well as from electrode ablation. This chemical species is commonly used for temperature measurement. The details about the measurements and the analyses methods are presented in ref. [8].

Nozzle entrance zone

- Without carbon injection, the C_2 rotational temperature depends on the arc intensity, but for a given intensity the rotational temperature is not influenced by the gas flow variation.
- With carbon injection, the C_2 rotational temperature seems to decrease with the carbon mass flow rate. At constant gas flow rate, the increasing of the carbon gas flow

rate raises the C/He ratio and then C_2 clusters are in the presence of an important density of solid carbon particles which inhibits their formation. This phenomenon is accentuated with a current of 350 A for which there is a high current density at the three electrode tips. At the high values of current, a strong erosion of the electrodes is observed as well as a scraping of small solid carbon particles, which are also an additional source of carbon increasing the C/He ratio and again inhibiting the formation of C_2.

For the low gas flow rates, although the C/He ratio increases, the process has a different behavior. In this case, by decreasing the gas flow rate, the enthalpy density is increased, involving higher plasma temperatures for the same electrical power input. In the same time, the residence time of the solid particles in the high temperature plasma zone increases. Thus, the carbon vaporization is improved and C_2 concentration as well as C_2 rotational temperature increase. However, due to the increase of the temperature gradient towards the graphite walls and the slow flow of the vaporized carbon towards the quenching zone, the carbon vapor condenses favorably on the graphite wall of the reactor and reduces the process effectiveness for the fullerene synthesis in gas-phase.

Thermodynamic calculations were performed to determine stable carbon species concentrations versus temperature. Solid carbon (graphite) is the stable carbon phase at temperatures lower than 4100 K. Above this temperature, carbon species are gaseous. C_2 temperature measurements show that the temperature in the nozzle entrance zone is greater than the condensation temperature of graphite whatever the operating conditions. Consequently, the conditions are favorable for carbon vaporization in the whole upper zone between the arc and the nozzle entrance.

5 PREPARATION OF THE FULLERENE SAMPLES

In the plasma process, insoluble carbon soot is generated together with soluble fullerenes. The fullerenes have been extracted from the fullerene soot with organic solvents (toluene) by applying Soxhlet-extraction. The C_{60} and C_{70} fullerene molecules present in the separated fractions have been qualitatively and quantitatively identified and measured by UV/VIS spectroscopy.

6 RESULTS AND DISCUSSION

The yield dependence on the most influential process parameters is presented in ref. [9]. To summarize, the nature of the plasma gas appears to be the most critical one. Yields have been found to be about one order of magnitude higher when using helium as plasma gas rather than argon or nitrogen, a fact generally known for the arc or laser process. The nature of the carbon precursor, showed no drastic influence on the process performance.

The novel results presented in this paper concern the study of the C/He ratio during the fullerene synthesis and the influence of this parameter on the fullerene yield and on the C_{70}/C_{60} ratio.

- Influence of the C/He ratio

The influence of the C/He ratio on the fullerene content and the C_{70}/C_{60} ratio are presented in Figures 3 and 4.

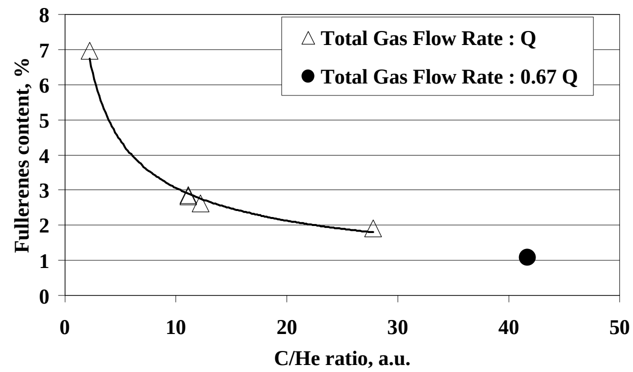


Figure 3: Influence of the C/He ratio on the fullerene content

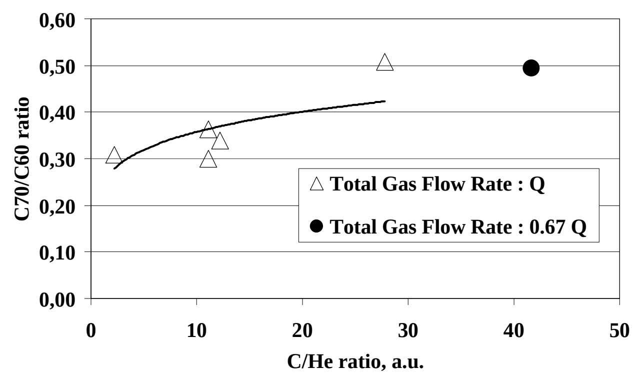


Figure 4: Influence of the C/He ratio on the C_{70}/C_{60} ratio

The fullerene content represents the weight fraction of all the fullerenes extracted by Soxhlet technique. To verify the reliability of the plasma process, three experimental runs with a C/He ratio of around 11 (arbitrary unit) have been performed. The two graphs show that a good reproducibility of the results is obtained.

The triangles symbols on the curves represent some samples obtained for five different experiments for which the operating conditions are the same excepted for the carbon mass flow rate. The filled points represent an experiment performed with the same operating conditions than the triangles at C/He = 28 but with a diminution of the plasma gas flow rate, Q by a factor of 0.67.

These figures show that when the C/He ratio increases, the fullerene content drops whereas the C_{70}/C_{60} ratio increases. A significant influence of the carbon mass flow rate on the fullerene yield is observed.

On the one hand, when increasing the carbon mass flow rate at a given gas flow rate, yield is reduced. But even if the yield appears lower, absolute production rate of fullerenes still increases when increasing carbon flow, if sufficient energy is available. On the other hand, when increasing the helium flow at a given carbon mass flow rate, yield is increased. In this case also, the process limitation is the energy provided to the gas by the plasma source. In conclusion of these results, to improve the performance of the plasma process for the production of fullerenes, it is important to reduce the C/He ratio for the fullerene yield and to increase the carbon mass flow rate for the productivity. The solution is to increase considerably the plasma gas flow rate, the limit being the energy provided by the plasma source (at a maximum current between 250 A and 300 A). In a next stage, the entire production system including periphery components will be further optimized to allow undercutting the present price of fullerenes and fullerene soot by a factor of ten in the medium term.

Concerning the influence of the C/He ratio on the C_{70}/C_{60} ratio, we can say that we have a behavior similar to the influence of the C/O ratio on the C_{70}/C_{60} ratio observed with the combustion process [2]. The higher the C/He ratio is, i.e. the higher the carbon concentration in the reactor, the higher the C_{70}/C_{60} ratio and the lower the C_{60} concentration. As concluded previously with the C_2 measurement, the influence of the C/He ratio on the C_2 concentration is the same. The higher the C/He ratio is, the lower the C_2 concentration. We can assume that the presence of C_2 in the high temperature zone of the reactor could contribute preferentially to the formation of C_{60} fullerenes.

7 FULLERENE SOOT

Fullerene soot (carbon-black-like nanoparticles with fullerenic surface structure) constitutes a completely new product family requiring intensive characterization and application testing. Plasma produced nanoparticles present some good reinforcement performances and are particularly well suited to be used as additives in various material applications like polymer composites and electrochemical components. Their commercial impact will of course be magnified if they can be the starting point of a new filler family. Performance fillers represent very important application volumes, where these new materials could progressively participate. Fullerene soot is of high interest for rubber reinforcing and as such for the tire and composite industry.

8 CONCLUSIONS AND PERSPECTIVES

The plasma process is addressing two types of products:

- Fullerenes, mainly C_{60} and C_{70},
- Fullerene soot based on carbon nanoparticles (carbon-black-like) with particular fullerenic surface structure.

So far the process of continuous fullerene synthesis is not fully optimized, but current yields typically of the order of 5% (toluene extractable) are obtained. At carbon flow rates of several hundred grams per hour, in extreme cases up to 1 kg/h, fullerene production rates of the order of 10 g/h can be obtained. No other technology has so far been able to reach such high fullerene production rates on a continuous basis and at atmospheric pressure.

The 3-phase AC plasma process can be considered as an improved highly flexible process with an enormous potential for further up-scaling to an industrial size and fullerene production at commercially viable cost. Major breakthroughs are expected through the implementation of a new operation mode at high gas flow rate, which will allow the treatment of a ten-fold product quantity at the present scale. Based on our knowledge of the pilot plasma process, an industrial unit based on the plasma technology will allow at a medium term the processing of 1 ton of fullerenes and 100 tons of fullerene soot per year, respectively and a reduction of the present price by a factor of ten is expected.

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