Synthesis of carbon blacks and fullerenes from carbonaceous wastes by 3-phase AC thermal plasma

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SYNTHESIS OF CARBON BLACKS AND FULLERENES FROM CARBONACEOUS WASTES BY 3-PHASE AC THERMAL PLASMA

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Abstract

In the current context of conventional fossil resource depletion, global warming and rising waste, thermal plasma appears as an interesting alternative compared to conventional thermochemical processes (combustion, gasification, pyrolysis, cracking…) in the fields of energy and nanomaterial synthesis.

The particular processing conditions due to thermal plasma (i.e. high temperatures and high enthalpy densities) allow using raw materials with Low Heating Value such as organic wastes (dried sewage sludge, plastics, used tires, sawdust…) or biomass (liquid, solid or gaseous) in the fields of energy and nanomaterial synthesis.

This paper reviews the last developments of a 3-phase AC plasma technology for the treatment of domiciliary and industrial wastes for nanomaterial synthesis, particularly the preliminary results reached for the production of carbon blacks and fullerenes from thermochemical processing by plasma of plastics (HDPE pellets) and carbon black soot resulting from tire pyrolysis.

Carbon blacks obtained from HDPE are well organized with physical characteristics similar to acetylene black and plasma treatment of tire carbon black soot shows that it is possible to produce fullerenes with this carbon precursor and with nitrogen plasma gas at atmospheric pressure.

1- INTRODUCTION

In the current context of conventional fossil resource depletion, global warming and rising waste, thermal plasma appears as an interesting alternative compared to conventional thermochemical processes (combustion, gasification, pyrolysis, cracking…) in the fields of energy and nanomaterial synthesis. Indeed, conventional methods based on Low Heating Value of the raw material present some limitations that might be overcome through plasma, particularly in terms of: material yield, gas purity, energy efficiency, dynamic response, compactness, flexibility... The injected plasma power can be adjusted independently of the heating value of the treated material. These particular processing conditions due to the thermal plasma (i.e. high temperatures and high enthalpy densities) allow using raw materials with Low Heating Value such as organic wastes (dried sewage sludge, plastics, used tires, sawdust…) or biomass (liquid, solid or gaseous) in the fields of energy and nanomaterial synthesis [1-2].
An original semi-industrial scale plasma technology using a three-phase AC source is presently working at the Centre PERSEE, MINES ParisTech, PSL. This technology has been developed initially for the synthesis of carbon nanoparticles such as fullerenes, carbon blacks, nanotubes… This technology has evolved since 1993 and has reached a high level of reliability, unique at this scale [3 - 5]. Since few years, this three phase AC plasma technology has been modified and adapted in order to operate as well as in neutral or reducing medium than under oxidizing conditions for waste and biomass valorization in the field of energy and nanomaterial synthesis [6].
This paper reviews the last developments of the 3-phase AC plasma technology for the treatment of domiciliary and industrial wastes for nanomaterial synthesis, particularly the preliminary results reached for the production of carbon blacks and fullerenes from thermochemical processing by plasma of plastics (HDPE pellets) and carbon black soot resulting from tire pyrolysis.

2- MATERIALS AND METHODS

Since 1993, researches on synthesis of carbon nanomaterials by plasma have been carried out at the laboratory of the Centre PERSEE - MINES-ParisTech - PSL in collaboration with academic and industrial partners (CNRS-PROMES France, Erachem Belgium and Timcal Belgium). For carbon nanoparticle synthesis, the originality of this plasma process consists in the substitution of the energy of the flame resulting of the incomplete combustion of a hydrocarbon by a thermal plasma in which a hydrocarbon precursor (gaseous, liquid or solid) is directly injected in order to crack it into carbon black and hydrogen. These researches have allowed the development of an original 3-phase AC plasma technology [3 - 5] at a pilot scale and a partnership with a Californian star-up (Monolith Materials) for the analysis and design of one pilot plant (in USA) for production of carbon black and hydrogen by thermal plasma [7]. This technology has evolved since 1993 and has reached a high level of reliability, unique at this scale.
The process set-up at Sophia-Antipolis at a pilot scale is illustrated in Figure 1. The process can be briefly described as follow: the plasma is powered by a 3-phase AC plasma power supply (600 Hz, 0-400 A, 263 kVA maximum power). Each of the three phases of the power supply is connected to the graphite electrodes of a 3-phase plasma torch located at the upper part of a reactor. Thermal plasma is generated by an arc discharge between the three graphite electrodes.

Carbon Black synthesis

In Figure 2 is represented the configuration used for the synthesis of carbon black (configuration 1 – solid line). For the treatment of plastic wastes (HDPE pellets), a special powder injection system is employed to mix the solid carbonaceous precursor with a suspending gas to transport the mixture inside the reactor. This aerosol flows across the plasma, reaching the highest temperature region in the reactor. Due to the high enthalpy density obtained, the plastic waste is cracking completely while passing through the plasma zone. The internal shape of the reactor has been designed to improve the conditions for cracking by a strong confinement of the gas flow. The internal part of the plasma reactor is composed of a high temperature insulator lining (solid graphite and graphite felt) in order to increase the heat density as well as to decrease the thermal losses from the hot gas through the walls. The external kiln of the reactor is a double wall water cooling cylinder. The system is equipped with a PTFE bag filter where product and gas are separated and collected. A gas network allows providing different plasma gases or mixtures (N_2, Ar, He, CO, H_2) to the plasma system. The process pressure is controlled to be at atmospheric pressure.

The pilot is composed of:

- a 100 kW 3-phase AC plasma torch with graphite electrodes, located on the upper part of the reactor,
- a high temperature reactive zone in which the plastic wastes (HDPE pellets) or carbon black soot resulting from tire pyrolysis (Powder) is injected with plasma gas,
- a hot wall reactive zone (2 meters high),
- a cooling and carrying zone,
- a filtration system where solid product (CB or fullerene soot) and gas (N_2-H_2 or N_2) are separated.

Figure 1: Overall picture of the 3-phase AC plasma reactor (2 meters high).

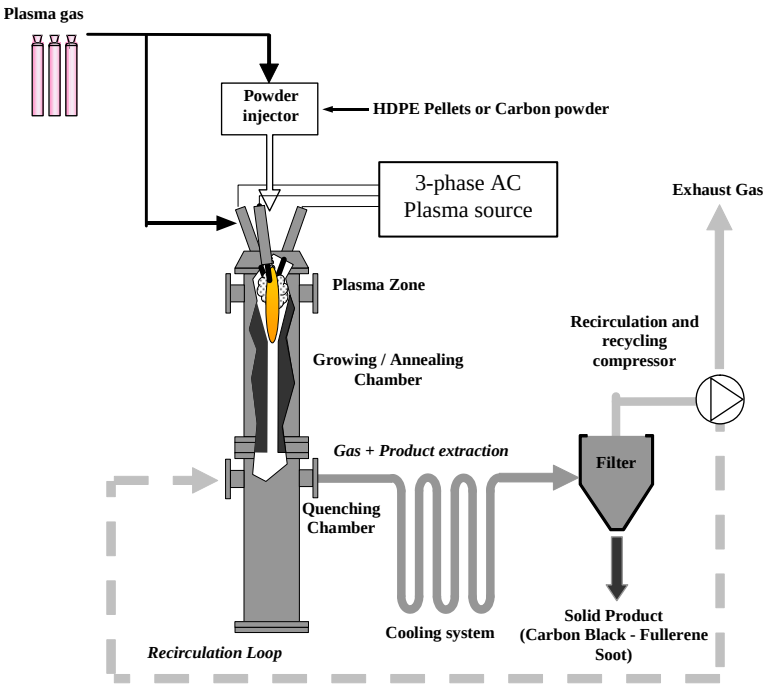

Figure 2: Scheme of the plasma reactor for the synthesis of carbon blacks (configuration 1 – solid line) and for the synthesis of fullerenes and nanotubes (configuration 2 – solid line + dashed line).

The plastic selected as feedstock for the test is a HDPE powder from Atofina : FINATHENE® 56020 S. This is a very high molecular weight high density polyethylene produced by the slurry loop low pressure polymerization process. It has been especially developed for the manufacturing of blow moulded rigid containers offering a high impact resistance and stackability behaviour (transport of dangerous goods). This grade can also be used in sheet extrusion and compression. FINATHENE® 56020 S is available as white powder (average particle size: 800 microns in a range 100 – 1600 microns and with a specific surface of 0.3 $m^2.g^{-1}$).
In Table 1 are summarized the main operating conditions for the synthesis of carbon black from HDPE used as carbonaceous precursor.

Property	Unit	Value
Average Power	kW	50
Average Current	A	220
Average Voltage	V	175
Plasma gas flowrate (N_2)	$Nm^3.h^{-1}$	2
Carrier gas flowrate (N_2)	$Nm^3.h^{-1}$	2
HDPE Flowrate	$Kg.h^{-1}$	0.25

Table 1: Main operating conditions for the synthesis of carbon black from HDPE used as carbonaceous precursor (average error ± 10%).

In the following chapter, this paper will present the most significant results about the characterization of the carbon black synthesized from HDPE using BET and SEM and a comparison between an industrial carbon black grade (Acetylene Black - Y50A - SN2A) and a HDPE plasma carbon black is proposed.

Fullerene synthesis

This 3-phase AC plasma technology, initially designed and optimized for the treatment of hydrocarbons and the synthesis of novel grades of carbon black, has been modified and adapted in order to process solid carbonaceous powder for the continuous synthesis of fullerenes, fullerene soot or carbon nanotubes [8 - 9]. The process combines the high temperature arc method with continuous gas-phase synthesis by injecting solid carbon precursors into a thermal arc plasma. The adaptations lead to the overall process scheme illustrated in Figure 2 (configuration 2 – solid line + dashed line). In this case, solid powder is carried away together with the plasma gas to the arc zone. The main difference with the classical arc process for fullerene and nanotube synthesis is that the input carbon rate is no more limited to the electrode erosion but can be controlled totally independently. 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 (dashed line in the Figure 2). The fraction that corresponds to the initial flow rate 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 operating conditions. 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} molecules,
• Fullerenic nanostructures based on carbon nanoparticles (carbon-black-like) with particular fullerenic surface structure.

The control of the three main processing parameters: temperature profile, residence time in the reactor and reactant concentration is of great importance to generate tailor-made particles. Thus, the system has been designed to adjust the residence time and the quenching rate by changing the gas extraction point from the reactor and the gas flow rate in the quenching/recirculation loop. The reactant concentration is adjusted by the control of the plasma gas/solid precursor ratio.

Experimental procedure for Fullerene synthesis

Today, the main processes applied in fullerenes production are the laser ablation, the arc discharge, arc jet plasmas, concentrated solar flux, resistive or inductive heating and combustion-based methods [10]. In the major part of these processes, the process is more or less the same and can be described as follow with the arc discharge as example: in the first step of the arc discharge, carbon vapor composed of atomic species and very small clusters is produced by the sublimation of carbon in an inert atmosphere through an electric arc maintained between two electrodes. In a second step, the carbon vapor is expended in an inert gas. In a third step, the carbon vapor is quenched and a part of the small clusters self-assemble to produce fullerenes.
As presented before, the plasma process for fullerene production is derived from the arc process but the main difference consists in injecting a carbon precursor as an aerosol (with nitrogen gas) through the 3-phase plasma. After traveling through the hottest temperature region (> 4000 K), the carbon is partially vaporized. The rate of the vaporized part of the carbon particles is function of the initial size of the particles and the residence time in the high temperature zone (plasma zone). After the re-condensation of the gaseous carbon on the non-vaporized part of the carbon precursor and an annealing step around 2000 K, the mixture of carbon nanoparticles and plasma gas is rapidly extracted from the hot region (quenching) and cooled down to room temperature by means of a gas recirculation loop which also contains the filtering system. The point of gas extraction from the reactor and the gas flow rate in the recirculation cycle determine the residence time of the carbon precursor in gas phase and the quenching rate.
Once collected in the filter, Soxhlet Toluene extraction was performed on the soot and the extract was analyzed by UV-Vis spectrophotometry. The extract concentration in fullerenes C_{60} and C_{70} was evaluated from the two absorption peaks at 330 nm and 470 nm [11].
In Table 2 are summarized the main operating conditions for the synthesis of fullerenes from carbon black soot resulting from tire pyrolysis used as carbonaceous precursor.

Property	Unit	Value
Average Power	kW	36
Average Current	A	180
Average Voltage	V	150
Plasma gas flowrate (N_2)	$Nm^3.h^{-1}$	4
Carrier gas flowrate (N_2)	$Nm^3.h^{-1}$	4
Carbon black soot flowrate	$Kg.h^{-1}$	0.8
Recirculation loop gas flowrate (N_2)	$Nm^3.h^{-1}$	200

Table 2: Main operating conditions for the synthesis of fullerenes from carbon black soot resulting from tire pyrolysis used as carbonaceous precursor (average error ± 10%).

In Table 3 are summarized the main characteristics of the carbon black soot resulting from tire pyrolysis (CCT-R 632 from Carbon Clean Tech) used as carbonaceous precursor.

Ingredient	Wt. %
Carbon black	80 – 90
Silica	1 – 5
Zinc oxide	1 – 5
Calcium oxide	1 – 5
Zinc sulphide	1 – 5

Table 3: Composition/information on ingredients (CCT-R 632 from Carbon Clean Tech MSDS).

3- RESULTS AND DISCUSSION

Carbon Black synthesis

TGA, BET and SEM analyses have been carried out on several samples taken in different locations in the reactor and the filter in the aim to analyse the particular structures of the plasma carbon blacks in function of the origin of the samples.
Plasma carbon blacks have been sampled in three zones of the process: sample A in the bag filter, sample B along the graphite walls of the reactor and sample C at the lower part of the reactor. In Table 4 are summarized the main results about these three samples, the raw material (HDPE pellets) and an industrial carbon black (Y50A acetylene carbon black from SN2A).

	Raw material (HDPE)	Sample A Bag Filter	Sample B Graphite Walls	Sample C Bottom of the reactor (1)	Y50A
BET ($m^2.g^{-1}$)	0.3	53.2	20.6	45	70 ± 10
Ash (wt %)		2.3	2.0	1.4	< 0.1

Table 4 : Characterization of the plasma samples.
(1) Sample contains HDPE-like particles. Product was sieved prior to testing but the finest particles could not be removed.

One can observed a small decrease of the specific surface area of the carbon black sampled on the surface of the inner graphite walls of the reactor (sample B). It is mainly due to the annealing of the carbon black deposit by the high temperature plasma during the process. One can observed too that the sample C contains some HDPE-like particles. These particles are the biggest HDPE pellets which have not been cracked during their processing due to the initial size of these particles and the residence times in the plasma zone which is not optimized for this kind of carbon precursor. Sample A is the more representative of the final product obtained from HDPE cracking by thermal plasma and its specific surface area is very interesting, in the range values of industrial carbon blacks like acetylene carbon black (Y50A).

Figure 3 represents a typical SEM image of some aggregates and agglomerates of HDPE carbon black synthesis by thermal plasma. Figure 4 represents a typical SEM image of some

aggregates and agglomerates of Y50A acetylene carbon black from SN2A. One can observe that both morphologies are very close, like previously observed on carbon black synthesis by thermal plasma from others various precursors (methane, ethylene, Pyrolysis Fuel Oil (PFO) or Colza Oil [5]).

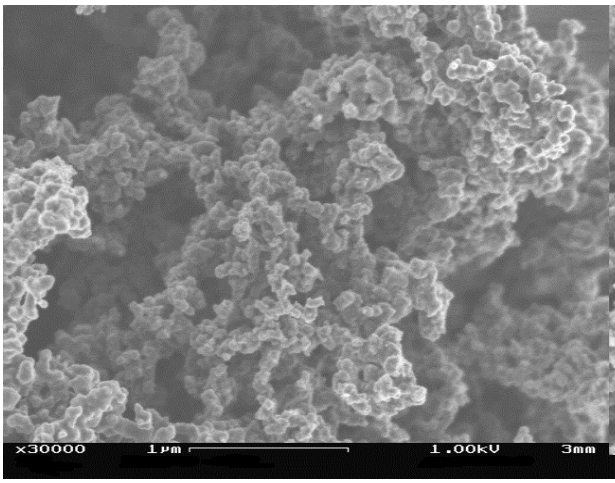

Figure 3: HDPE Plasma Carbon Black (Sample A).

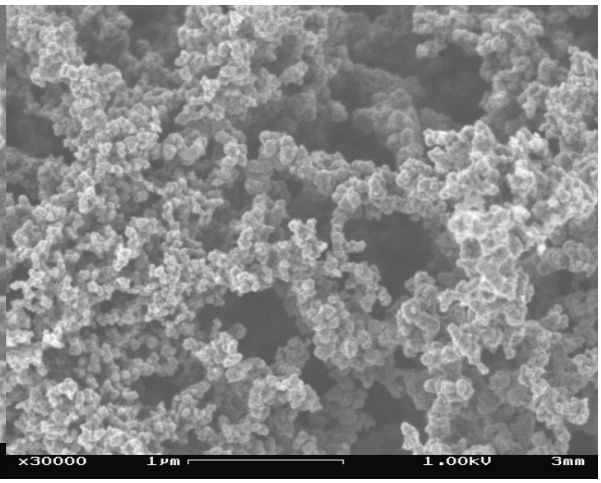

Figure 4: Y50A Carbon Black.

This is one of the particularities of the 3-phase AC thermal plasma carbon blacks. Independently of the carbon precursors, the carbon blacks produced are always very similar morphologies due to the thermal history of the carbon particles in the reactor which is not only function of the carbon precursor but mainly of the temperature of the thermal plasma and the nature of the plasma gas. The structure of the plasma CBs is the result of the growing of the particles at some temperatures between 1800 K and 2500 K. The 3-phase AC plasma process allows the production of new carbon grades thanks to reaction conditions unreachable by the conventional combustion processes.

Fullerene synthesis

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.

In Table 5 are given the wt % of C_{60} and C_{70} measured after the plasma treatment with nitrogen plasma gas.

	C_{60}	**C_{70}**	**$C_{60} + C_{70}$**
wt %	0.787	0.137	0.924

Table 5: wt % of the C_{60} and C_{70} fullerenes synthesized by 3-phase AC thermal plasma with nitrogen plasma gas.

Previously [10], during the processing of carbon power (CB or graphite powder) by 3-phase AC thermal plasma, best yields were obtained using helium as plasma gas, slightly lower with argon while nearly no fullerenes were found with nitrogen. These results were in line with

results obtained with other high temperature methods (arc, laser or solar). In the case of nitrogen, this was probably due to the formation of stable binary species at high temperature, such as CN, which stops the production of carbon vapor species (C, C_2, C_3 …) as these clusters have been identified as fullerenes precursors. In the present case, the impurities in the carbon precursor could play the role of catalyst promoting the formation of fullerenes during the plasma treatment. In the literature, it is the first time such fullerene yields are synthesized with nitrogen plasma gas at atmospheric pressure.

So far the process of continuous fullerene synthesis is not fully optimized, but current yields typically of the order of 1 % (toluene extractable) have been obtained. At carbon flow rates of several hundred grams per hour, fullerene production rates of the order of 10 $g.h^{-1}$ could be achieved.

4- CONCLUSIONS

3-phase AC plasma systems open a new area for the production of carbon nanostructures. These technologies are characterized by a very high versatility and flexibility. It has been demonstrated in several papers that the very similar technology can be used for the production of a wide range of carbon nanostructures ranging from carbon black over fullerenes to carbon nanotubes with a high product selectivity. In addition, plasma systems allow the conversion of any organic carbon precursor: liquid, solid or gaseous to valuable carbon nanostructures.
This paper reviews the last developments of the 3-phase AC plasma technology for the treatment of domiciliary and industrial wastes for nanomaterial synthesis, particularly the preliminary results reached for the production of carbon blacks and fullerenes from thermochemical processing by plasma of plastic wastes (HDPE pellets) and carbon black soot resulting from tire pyrolysis. Carbon blacks obtained from HDPE are well organized with physical characteristics similar to acetylene black and plasma treatment of tire carbon black soot shows that it is possible to produce fullerenes with this carbon precursor and with nitrogen plasma gas at atmospheric pressure.

Carbon Black: The main difference with other gas-phase synthesis processes (mainly combustion processes) is that the enthalpy applied to the system can be controlled totally independently by means of an external electric power supply. As a consequence, this allows the creation of thermodynamic conditions unreachable by conventional means. In particular, very high temperatures can be obtained (higher than 3,000 K up to 10,000 K) thus allowing the formation of specific species (C_1, C_2, etc), which could play an important role as precursor for new carbon black grades. In the conventional carbon black market, it will allow the use of new raw materials, such as waste oils, vegetable oils, etc, a more rational use of the raw material (100 % carbon yield), the production of carbon black free from CO_2 emission on the site and the production of hydrogen as by-product.

Fullerenes and fullerene soot: 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 structures.

So far the process of continuous fullerene synthesis from carbon black soot resulting from tire pyrolysis is not fully optimized, but current yields typically of the order of 1 wt % (toluene extractable) are obtained. At carbon flow rates of several hundred grams per hour, fullerene production rates of the order of 10 $g.h^{-1}$ could be achieved. No other technology has so far

been able to reach such high fullerene production rates on a continuous basis at atmospheric pressure and with nitrogen.
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.

In the emerging domains, the plasma process will allow the production of carbon materials of nano-sized structure from carbonaceous wastes, which are without any doubt amongst the most promising resources for future industrial applications and 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.

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