Synthesis of Carbon Blacks from HDPE plastic by 3-phase AC thermal plasma

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Abstract: This paper reviews the last results obtained on the 3-phase AC plasma technology developed at the Centre PERSEE, MINES ParisTech, PSL for the treatment of domiciliary and industrial wastes for nanomaterial synthesis with a special focus on preliminary results obtained for the production of carbon blacks from plastics (HDPE pellets). Carbon blacks obtained from HDPE have shown a highly nanostructured organization very similar to those of acetylene black.

Keywords: Carbon Black, Plastic Wastes, Thermal Plasma, Material Recycling.

1. Introduction

Global production of carbon black was around 7 million tons in 1993 [1], 10 million tons in 2005 [2], 11 million tons in 2012 [3] and over 12 million tons in 2015 [4]. The carbon black demand is in constant growing due to its use as a key element in tires, conductive plastics, batteries (laptops and smartphones). The main processes used for the synthesis of carbon black are thermal processes (Furnace black, thermal black ...) that require the incomplete combustion of a large part of the carbon precursor to provide the energy required for cracking the remaining part. Therefore, they are characterized by a high level of CO_2 emissions (0.125 % of the total CO_2 emissions [5]) and actively participate in global warming. The use of plastic wastes could allow the production of carbon black by cracking but their treatment requires high energy densities together with high temperatures. In the current context of conventional fossil resource depletion, global warming and rising waste, thermal plasma appears as an interesting option versus conventional thermochemical processes (combustion, gasification, pyrolysis, cracking…) in the fields of energy and nanomaterial synthesis. Indeed, conventional methods based on poor Low Heating Value raw materials present some limitations that might be overcome through plasma, particularly in terms of: yields, 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 brought by 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 [6 - 9].

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 [10 - 12]. 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 [9].

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 plasma carbon blacks from plastics (HDPE pellets).

2. The 3-phase AC plasma process

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. 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.

The process set-up 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 on the upper part of a reactor. Thermal plasma is generated by an arc discharge between the three graphite electrodes.

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 cracked in quasi totality 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.

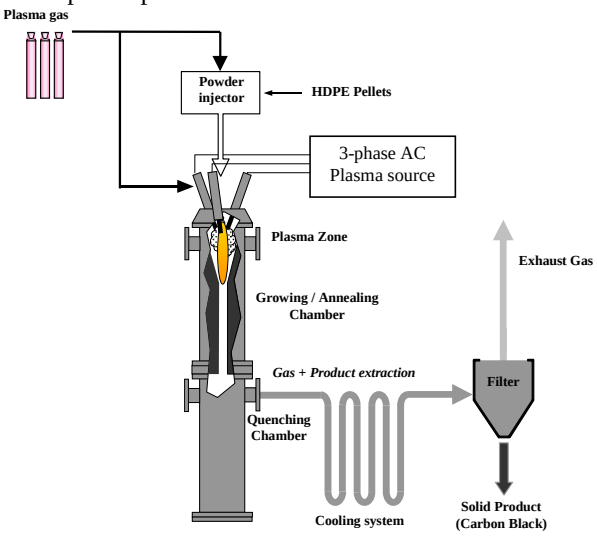

Fig. 1. Scheme of the 3-phase AC plasma process for the synthesis of carbon blacks from HDPE pellets.

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 waste (HDPE pellets) is injected with the plasma gas,
- a hot wall reactive zone (2 meters high),
- a cooling and carrying zone,
- a filtration system where solid product (Carbon Black) and process gas (N_2-H_2 or N_2) are separated.

The plastic selected as feedstock for the test is a HDPE powder from Total : FINATHENE® 56020 S. This is a very high molecular weight high density polyethylene produced by the slurry loop low pressure polymerization process. 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.

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

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

In Table 2 are summarized the main inorganic elements present in the HDPE pellets (FINATHENE® 56020 S) used as carbonaceous precursor. Chemical analyses of the inorganic impurities have been done by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Analyses show that HDPE is a product with a high purity. The main inorganic impurities (Silicon and Aluminum) do not exceed 50 ppm and the average values for the other inorganic impurities are around 1 ppm.

Table 2. Inorganic impurities present in the HDPE pellets (FINATHENE® 56020 S) used as carbonaceous precursor (mean percentage error ± 1.5 %).

Chemical Characteristics	Value	Unit	Chemical Characteristics	Value	Unit
Si	42	ppm	V	1.1	ppm
Zn	<0,1	ppm	Cd	<0.1	ppm
Al	15.1	ppm	Co	<0.1	ppm
Ca	0.8	ppm	Cu	0.1	ppm
Fe	0.1	ppm	Mn	<0.1	ppm
K	<0.1	ppm	Ni	<0.1	ppm
Mg	0.1	ppm	Cr	2.0	ppm
Na	0.3	ppm	Sb	<0.1	ppm
Mo	<0.1	ppm			

In the following section, this paper will present the most significant results about the characterization of the carbon black synthesized from HDPE using Nitrogen Sorption (Brunauer–Emmett–Teller - BET), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). A comparison between an industrial carbon black grade (Acetylene Black - Y50A - SN2A), the carbonaceous precursor (HDPE) and three HDPE plasma carbon black samples is proposed.

3. Results and discussion

BET, SEM and TGA 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 inner graphite walls of the reactor and sample C at the

lower part of the reactor. In Table 3 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).

Table 3. Specific surface area values for three plasma carbon black samples, HDPE pellets and Y50A acetylene carbon black from SN2A (mean percentage error ±0.5 %).

	Raw material (HDPE)	**Sample A**	**Sample B**	**Sample C [(1)]**	**Y50A**
BET ($m^2.g^{-1}$)	0.3	53.2	20.6	45	70 ± 10

[(1)] Sample contains HDPE-like particles. Product was sieved prior to testing but the finest particles could not be removed.

One can observe 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 also observe that the sample C contains some HDPE-like particles. These particles are the biggest HDPE pellets which have not been cracked during their plasma processing due to the initial size of these particles and residence time in the plasma zone which is not suitable. 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 2 represents a typical SEM image of some aggregates and agglomerates of HDPE carbon black synthesis by thermal plasma. Figure 3 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 [12]).

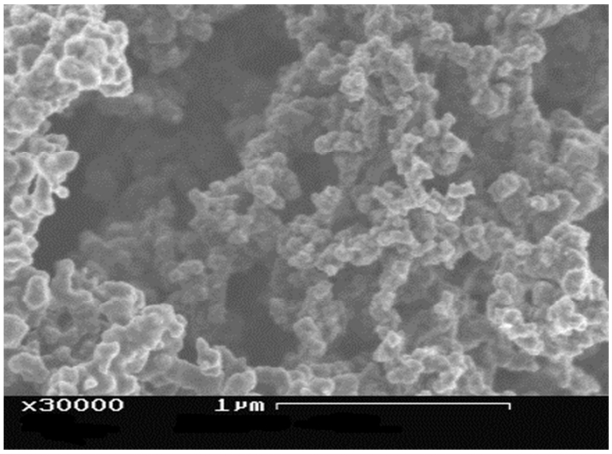

Fig. 2. HDPE Plasma Carbon Black (Sample A).

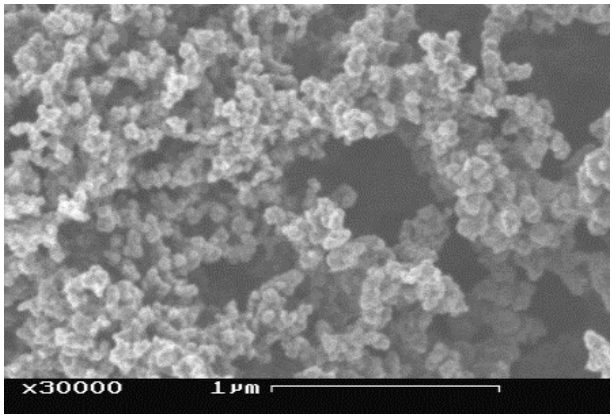

Fig. 3. Y50A Carbon Black.

Figure 4 presents the TGA curves obtained for the three plasma carbon back samples, the HDPE pellets and the industrial carbon black sample (Y50A).

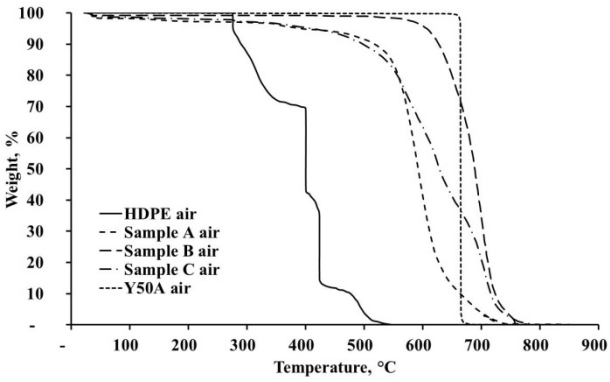

Fig. 4. TGA curves obtained for the three plasma carbon back samples, the HDPE pellets and the industrial carbon black sample (Y50A). TGA conditions: 900°C in air @ 30°C.min^{-1} HR5, S1

The specific method applied is one with a heating rate of 30°C.min^{-1} in air, resolution factor 5 and sensitivity factor 1. The curves of the samples A and C show a smooth slope corresponding to the small part of the HDPE pellets which has not been totally cracked during the plasma treatment. It is not the case for the sample B which is stayed during a long period of time at high temperature (> 2000 K). The strong decreasing of the curve of the sample A at around 600 °C (from 580 °C to 620 °C for 80 % of the sample) shows that this product is homogeneous and presents a well organised structure. It is the same thing for the curve of the sample B but at a higher temperature (between 650 °C and 720 °C for 90 % of the sample) corresponding to a homogeneous product more graphitised. One can also observed that sample B is structured to a higher degree than Y50A, whose the combustion temperature is around 670 °C. For the sample C, the strong decreasing starts at the same temperature than the sample A (580 °C) and finished the same

temperature than the sample B (720 °C) showing a product well graphitised but inhomogeneous more or less composed of a mixing of the A and B carbon blacks. The results of these TGA analyses show that the plasma process allows producing carbon blacks with a well organised nanostructure but it has to be optimised concerning the residence time of the HDPE in the high temperature zone in the aim to better control the homogeneity of the plasma carbon black and to totally crack all the HDPE injected.

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 some 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 temperatures ranging from 1800 K up to 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.

4. Conclusions

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 high product selectivity. In addition, plasma systems allow the conversion of any organic carbon precursor: liquid, solid or gaseous to valuable carbon nanostructures. 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, ...), 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, ... with 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.

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 from thermochemical processing by plasma of plastic wastes (HDPE pellets). Carbon blacks obtained from HDPE are well organized with physical characteristics similar to acetylene black.

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.

5. References

[1] J.B. Donnet, R. C. Bansal, M. J. Wang, Carbon Black, Second Edition, Revised and Expanded, ISBN 0-8247-8975-X, Ed. MARCEL DEKKER, (1993)

[2] J.-F. Auchter, Chemical Economics Handbook: Carbon Black, Menlo Park, CA, SRI Consulting, (2005).

[3] Carbon Black Sales Website - http://carbonblacksales.com/worldwide-carbon-black-market-12-million-metric-tons-2015/

[4] Carbon Black User's Guide: Safety, Health, & Environmental Information, International carbon black association (March 2016) - http://www.carbon-black.org/index.php/carbon-black-uses/carbon-black-user-s-guide

[5] Trends in global CO_2 emissions, PBL Netherlands Environmental Assessment Agency, report, (2015)

[6] F. Fabry, C. Rehmet, V. Rohani, L. Fulcheri: Waste gasification by thermal plasma: a review. Waste and Biomass Valorization, **4**, 3, 421-439 (2013)

[7] E. Gomez, D. Amutha Rani, C.R. Cheesemen, D. Deegan, M. Wise, A.R. Boccaccini: Thermal plasma technology for the treatment of wastes: a critical review. J. Hazard. Mater. **161**, 614-626 (2009)

[8] H. Huang, L. Tang: Treatment of organic waste using thermal plasma pyrolysis technology. Energ. Conv. And Manag. **48**, 1331-1337 (2007)

[9] S. Takali, F. Fabry, V. Rohani, F. Cauneau, L. Fulcheri: Development of a 100 kW plasma torch for plasma assisted combustion of low heating value fuels. J. of Phys.: Conf. Series 550 012018 (2014)

[10] F. Fabry, G. Flamant, L. Fulcheri: Carbon black processing by thermal plasma. Analysis of the particle formation mechanism. Chem. Eng. Sc. **56**, 6, 2123-2132 (2001)

[11] L. Fulcheri, N. Probst, G. Flamant, F. Fabry, E. Grivei, X. Bourrat: Plasma processing: a step towards the production of new grades of carbon black. Carbon **40**, 2, 169-176 (2002)

[12] N. Probst, E. Grivei, F. Fabry, L. Fulcheri, G. Flamant, X. Bourrat, A. Schroder: Quality and performance of carbon blacks from plasma process. Rubber Chem. and Techn. **75**, 5, 891-906 (2002)