11º Workshop em Engenharia e Tecnologia Espaciais
18, 19 e 20 de agosto de 2020

Thermal plasma technology: a feasible way to produce advanced carbonaceous materials

Eduardo Sant'Ana Petraconi Prado [1, 2,*], Felipe de Souza Miranda [2], Gisele Amaral [1], Gilberto Petraconi [2], Maurício Ribeiro Baldan [1]

[1] Instituto Nacional de Pesquisas Espaciais - INPE, Rua dos Astronautas 1758, Postal Code 12227-010 São José dos Campos, SP – Brazil.

Aluno de Doutorado do curso de Ciência e Tecnologia de Materiais e Sensores - CMS.

[2] Instituto Tecnológico de Aeronáutica - ITA, Rua Marechal Eduardo Gomes 50, Postal Code 12228-900 São José dos Campos, SP – Brazil.

* Corresponding author.

E-mail address: edu.petraconi@gmail.com

Abstract. *A significant, valuable percentage of waste stream produced on a large scale in the industries, consists of high carbon content materials. Currently, the lack of cost-effective recycling technology made the thermal plasma treatment a viable means for recycling these materials. Beyond that, the thermal plasma can convert the residues into nanostructured materials, with high potential for applicability in the aerospace sector. The viability of using thermal plasma for waste treatment/processing was demonstrated in the present study. For this, the coal tar pitch was selected to be treated using a thermal plasma system. The system is composed of a reactor coupled with a non-transferred arc plasma torch, wich the coal tar pitch is injected in the center of the high enthalpy plasma jet generated by the plasma torch. The preliminary results from the initial set of experiments were analyzed using the characterization methods, such as scanning electron microscopy (FEG-SEM), X-ray diffraction, and Raman spectroscopy showing that the route through thermal plasma processing is promising for the production of the advanced carbonaceous materials with high aggregate value.*

Keywords: Thermal Plasma; Coal Tar Pitch; Treatment; Carbonaceous Materials.

1. Introdução

Currently, in the industrial field, the implementation of new technologies for the processing of various types of waste is fundamental, aiming the environmentally and economically correct final waste disposal [Bulatov and Klemes 2009]. Coal tar pitch is a waste with a high carbon content produced on a large scale in the steel industries, highly polluting to the environment because it consists essentially of aromatic hydrocarbons [Zhang et al 2020].

Thermal plasma processing of waste with high carbon content has been promising for its potential of energy generation (combustible gases) and products of high added value (advanced carbonaceous materials) [Mohsenian et al 2016]. The main advantages of thermal plasma for wastes processing are the choice of unique properties associated with thermal plasmas, namely high specific heat, high thermal conductivity, a variable electrical conductivity, and high emission of radiation.. The plasma generators have essentially two functions, which is the transformation of electrical energy into thermal energy, and transfer the energy to the material [Samal 2020].

In this scenario, the present study has the objective of development and use of a Prototype of a thermal plasma reactor for the processing of the coal tar pitch, designated as Pitch 110, supplied by Companhia Siderúrgica Nacional (CSN), aiming to evaluate the plasma process and its production efficiency of advanced carbonaceous materials, with a focus on obtaining carbon nanostructures such as carbon black, carbon nanotubes and graphene oxide. Admittedly, the aerospace sector is a strong supporter of this situation, motivating, for example, the synthesis of new materials by powder metallurgy, shaping of materials in the form of nanostructured composites, developments of light structures, electronic components, as well as surface mechanical treatments in order to obtain the most suitable properties.

Therefore, this work shows the preliminary results of the initial experiments, proving that this project is highly relevant for the management of coal tar pitch and a new source for obtaining advanced carbonaceous materials.

2. Experimental materials and methods

2.1 Raw material

The raw material used in this work is the Coal Tar Pitch (CTP) from Companhia Siderúrgica Nacional (CSN), which has a softening point between 107–113 ºC. The physicochemical characterizations of the base material are shown in Table 1; tests were performed following standards ASTM International (American Society for Testing and Materials). CTP is produced by Companhia Siderúrgica Nacional (CSN) in Brazil.

Table 1. Results of physicochemical characterizations of raw CTP.

Test	Units	Value	Specification
Element	(wt. %)		
C		87.8	ASTM D5291 (ASTM 2015)
H		5.18	ASTM D5291 (ASTM 2015)
N		0.9	ASTM D5291 (ASTM 2015)
S		0.51	ASTM D4239 (ASTM 2014)
O		5.54	ASTM D3176 (ASTM 2015)
Ash content	(wt. %)	0.07	ASTM D482 (ASTM 2013)
Water content	(vol. /wt. %)	4.4	ASTM D95 (ASTM 2013)
Heating power	(MJ/kg)		ASTM D240 (ASTM 2014)
Upper		35.96	
Lower		34.86	

Initials experiments

The initial experiments were carried out with a processing time set at 30 min and included the following components: non-transferred arc plasma torch, pitch injector, process reactor, and particulate separator (cyclone) shown in Figure 1. The operating parameters of the plasma torch were fixed at the current and voltage of 130 A and 70 V, respectively. The plasma torch consists of two vortex chambers with a working gas flow rate in the first chamber with 90 liters/min of N_2 and in the second chamber with 30 liters/min of compressed air. The coal tar pitch was inserted into the reactor with a flow rate was 30 mL/min through a continuous feeding system that includes a pressure vessel with a maximum capacity of 1 liter and atomized injection nozzle. Argon was used as the carrier gas and the pressure of 3 bar for the transport of pitch at room temperature.

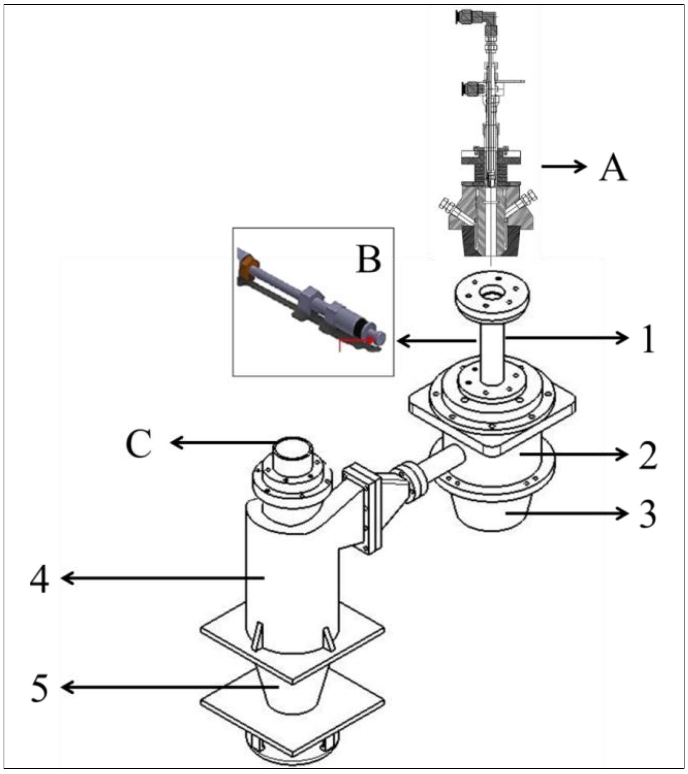

Figure 1. The processing system (A- Plasma torch, B- Injector nozzle, C- Gas treatment system, and 1 to 5 material collection chambers).

Characterization

The morphology of the samples was analyzed by Field Emission Gun Scanning Electron Microscopy *FEG*-SEM (Mira 3 Tescan) using the secondary electrons detector. The critical structure of carbon particles was recorded by X-ray diffraction (X'Pert Powder diffractometer - Panalytical), with a step size of 0.02°, 2θ range of 15–90°, and step time of 10 s. Raman scattering spectroscopic analysis was employed to determine the chemical compositions of the advanced carbonaceous materials using a Renishaw 2000 spectrometer

(Renishaw), with excitation wavelengths in the visible spectrum (514 nm) and two accumulations.

2.2 The process of production advanced carbonaceous materials

The proposal of the project is the realization of several experiments at the plasma reactor of the Laboratório de Plasma e Processos of Instituto Tecnológico de Aeronáutica (LPP-ITA), ranging the power of a non-transferred plasma torch between 5 to 15 kW and using different working gas (N_2, Ar and air). The main elements of the experimental system are shown in the process flowchart (Figure 2).

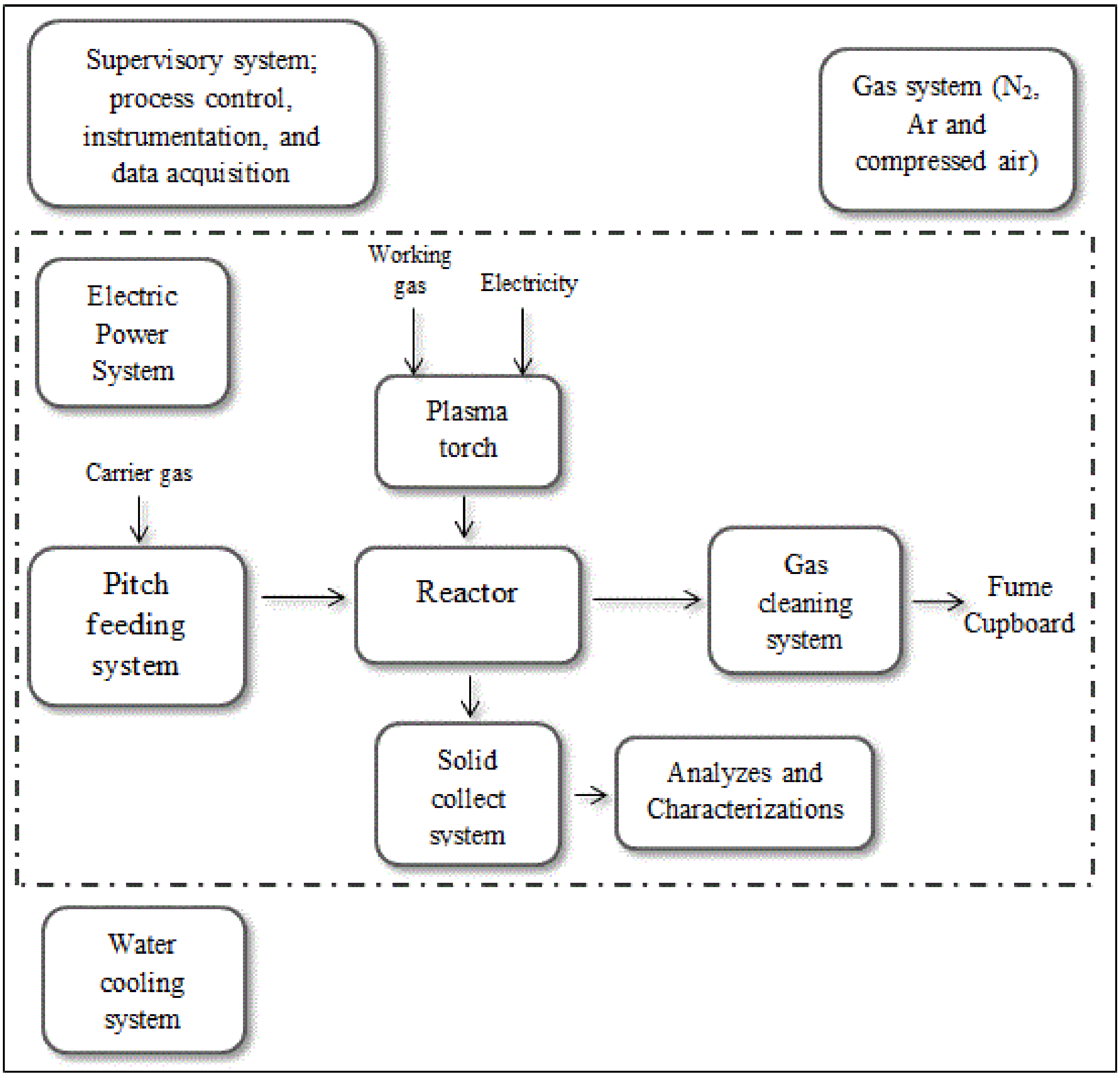

Figure 2. Experimental system for the evaluation of the coal tar pitch processing.

3. Preliminary results

Figure 3 shows the system and the respective materials obtained after the coal tar pitch processing.

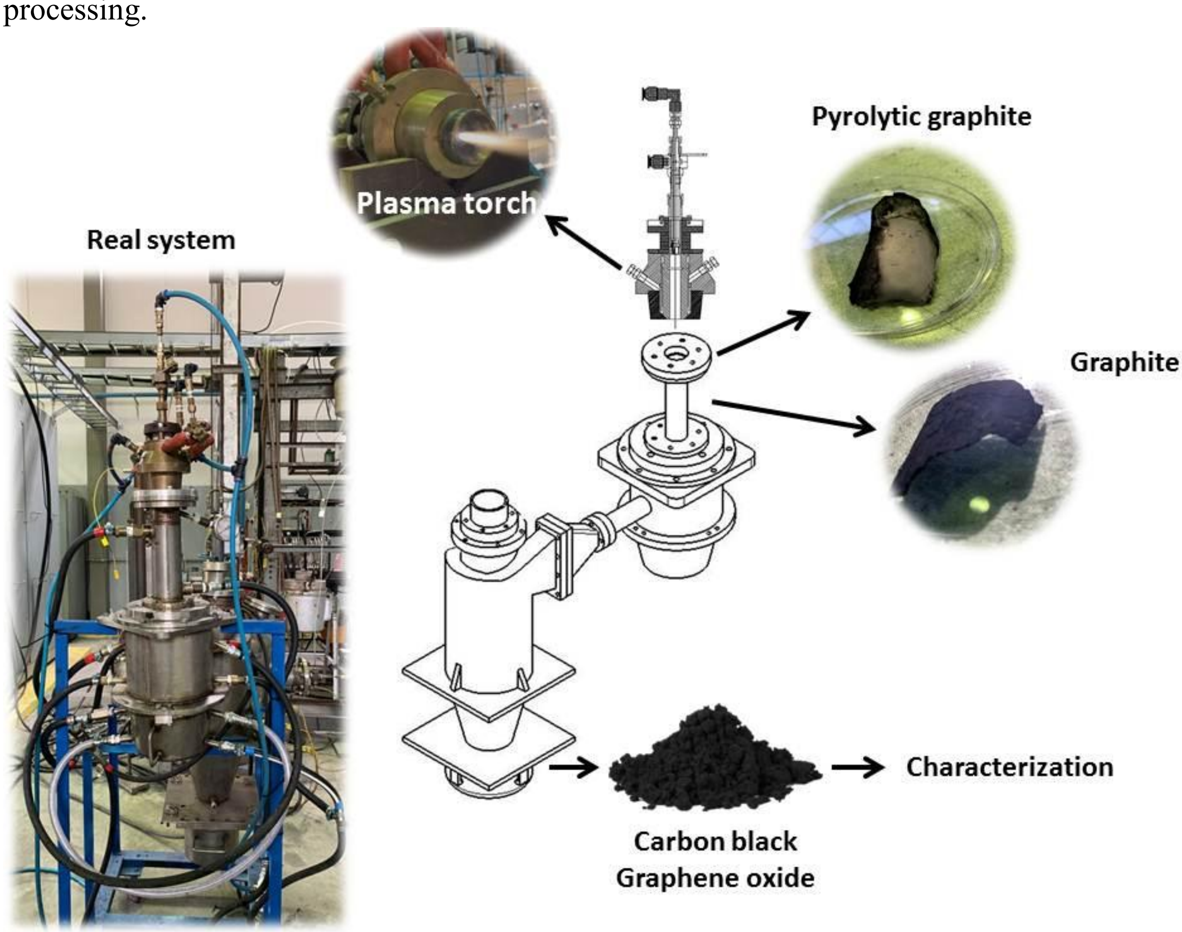

Figure 3. System and products obtained from the processing of coal tar pitch.

Among the carbonaceous materials highlight:

• Graphite: It is produced due to deposition on the reactor walls during the process [Guo and Kim 2010];

• Pyrolytic graphite: Obtained in high-temperature regions (> 1800 ° C) as in the upper part between the torch and reactor coupling. Due to the deposition of graphite on the wall, the passage channel of the plasma jet is restricted, consequently increasing the local temperature forming the Pyrolytic Graphite which has a silvery aspect [Paredes et al 2000];

• Graphene oxide: obtained due to the conversion of the carbonaceous components of the pitch into graphite and its subsequent reduction during exposure to thermal plasma and oxidizing environment [Liu et al 2020];

• Carbon black produces a temperature in the range of 1300-1600 K and is annealed in the region of electric arcs due to fluid recirculations [Guo and Kim 2010].

Microstructural investigations

In Figure 4 are presented imagens of the carbon black sample, in Figure 4 (A and B) the quasi-spherical were observed, with a size range between 30 to 60 nm. With higher magnification (Figure 4 (C), smaller particles can be observed (~30 nm).

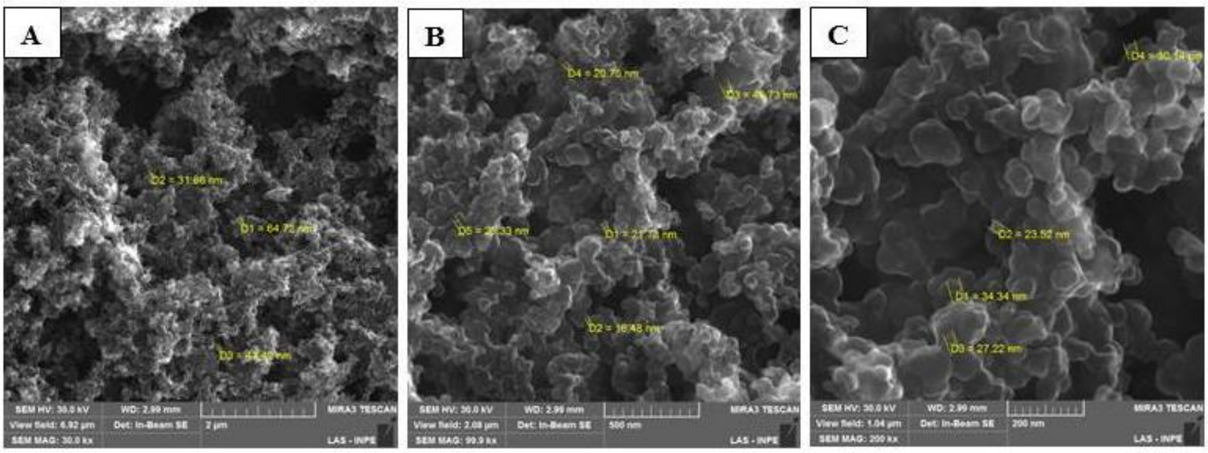

Figure 4. *FEG*-SEM images of thermal plasma processing product of CTP.

Structural identification

Figure 5 presents the XRD pattern of the material obtained. There are characteristics peaks centered at ~ 25,5º and ~ 43º, which were assigned to the (002) and (100) planes of carbon black [Vicentini et al 2016] and the peaks are in agreement to the study by [Sahu et al 2013]. These peaks correspond to interplanar distances of 3.5 and 2.1 Å, respectively.

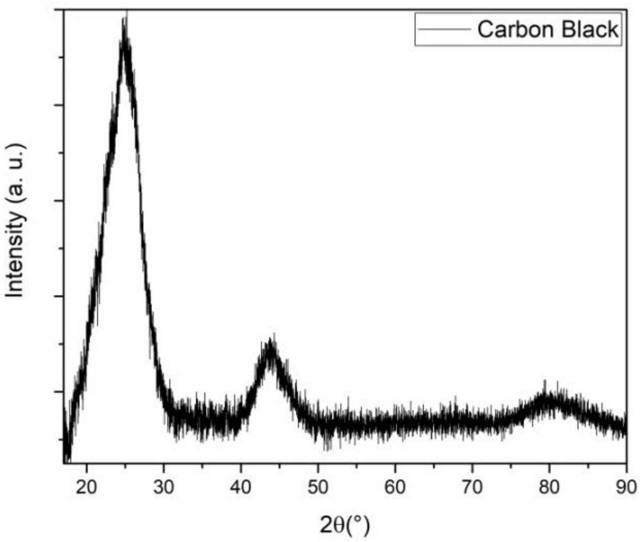

Figure 5. X-ray diffraction pattern of thermal plasma processing product of CTP.

Carbon structure

The Raman spectra of carbon black obtained by thermal plasma processing represented in Figure 6 show a higher degree of three-dimensional ordering, consisting of two main bands observed at ~1340 and 1560 cm^{-1}, indicated as band D and G, respectively.

These results are the first step in the design of a new process of clean industrial plasma for the synthesis of carbon black from the coal tar pitch.

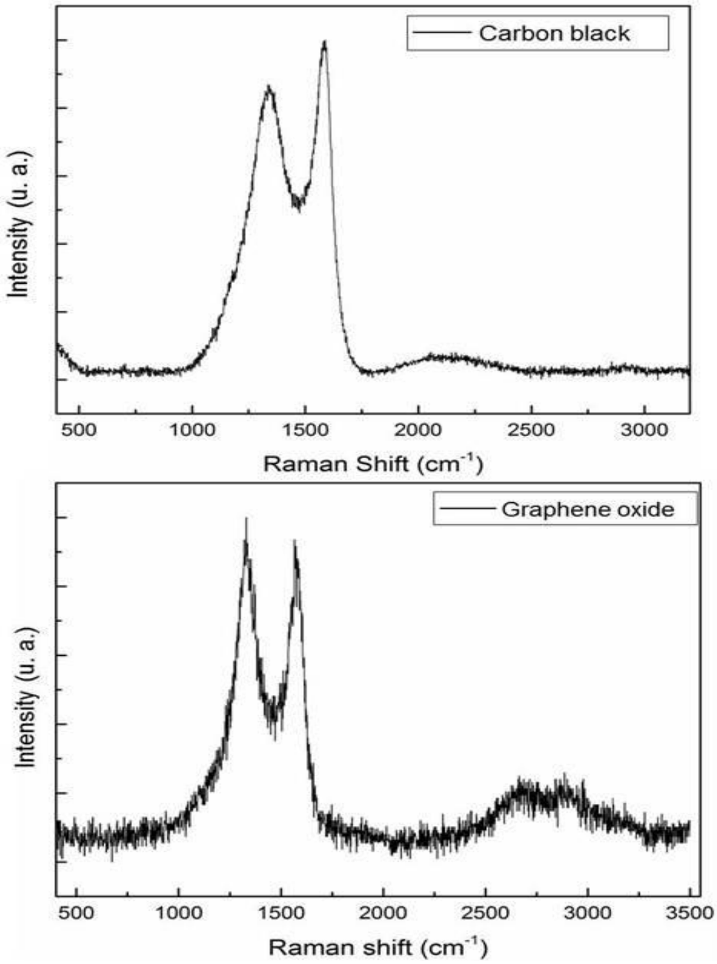

Figure 6. Raman spectra of thermal plasma processing products of CTP: (a) carbon black (b) graphene oxide.

Although in small quantities and mixed with carbon black, traces of graphene oxide production were found. The typical bands G at ~1601 cm^{-1} and D at ~1346 cm^{-1}, from E_{2g} mode first-order scattering in graphene and breathing mode of aromatic rings (very intense and broad) are identified [Perez et al 2019]. Besides, the weak overtones region with signals at 2686, 2938, and 3184 cm^{-1} are distinguished. Within these experimental conditions, of course, it is possible to optimize the process with parameter variation to obtain the greater quantity and higher the intensity signal coming from graphene oxide, preserving the intensity ratio ID/ IG ~ 1.

4. Conclusion

The application of thermal plasma technology in waste treatment for the production of advanced carbonaceous materials is still the object of study, due to the high complexity of process optimization. Nowadays industries face the challenge of developing environmentally and economically viable routes for their waste. In this scenario, it can be concluded that this project is very important for the management and disposal of coal tar pitch; also, it is important to mention that the enormous technical/scientific challenge for producing advanced carbonaceous materials with high added value. Tests will be carried out to identify the main limitations and advantages in the production process of carbonaceous materials compared to other technologies, besides varying processing parameters such as electrical power, working gas, and addition of catalysts. In these tests, all the variable of the process will be evaluated according to the nanostructured materials obtained, considering the characterization techniques reported in the literature. The project perspective is to obtain materials with similar characteristics of products already industrialized, with potential for application in the aerospace sector.

Acknowledgment: *The authors acknowledge the Plasma and Process Laboratory of the Aeronautics Institute of Technology (LPP-ITA) and Associated Laboratory of Sensors and Materials of the National Institute for Space Research (LABAS-INPE).*

References

Bulatov, I. and Klemes, J. (2009) "Towards cleaner technologies: emissions reduction, energy and waste minimisation, industrial implementation." In: Clean Technologies and Environmental Policy.

Guo, X. F. and Kim, G. J. (2010) “Synthesis of ultrafine carbon black by pyrolysis of polymers using a direct current thermal plasma process.” In: Plasma Chemistry and Plasma Processing, 30(1), 75-90.

Liu, S., et al (2020) “Pitch derived graphene oxides: Characterization and effect on pyrolysis and carbonization of coal tar pitch.” In: Journal of Analytical and Applied Pyrolysis, 145, 104746.

Mohsenian, S., et al. (2016) “Hydrogen and carbon black nano-spheres production via thermal plasma pyrolysis of polymers.” International Journal of hydrogen energy, 41(38), 16656-16663.

Paredes, J. I., et al. (2000) “Comparative study of the air and oxygen plasma oxidation of highly oriented pyrolytic graphite: a scanning tunneling and atomic force microscopy investigation.” In: Carbon, 38(8), 1183-1197.

Perez, L. A., et al (2019) “Raman spectroscopy coupled with AFM scan head: A versatile combination for graphene oxide/reduced graphene oxide hybrid materials.” In: Applied Surface Science, 495.

Sahu, V., et al. (2013) “Synthesis of hydrophilic carbon black; role of hydrophilicity in maintaining the hydration level and protonic conduction” In: RSC advances, 3(12), 3917-3924.

Samal, S. (2020) “Thermal Plasma Processing of Materials: High Temperature Applications.”

Standard Practice for Ultimate Analysis of Coal and Coke (2015)

Standard Test Method for Ash from Petroleum Products (2013)

Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (2014)

Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion (2014)

Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation (2013)

Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants (2015)

Vicentini, F. C., et al. (2016). Nanostructured carbon black for simultaneous sensing in biological fluids. Sensors and Actuators B: Chemical, 227, 610-618.

Zhang, Y., et al. (2020) “Emission characteristics and potential toxicity of polycyclic aromatic hydrocarbons in particulate matter from the prebaked anode industry.” In: Science of the Total Environment, p. 137546.