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REVIEW

OPTICAL PROPERTIES OF SOME CARBON TYPES

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The aim of this study is to review the application of the petrographic research, as a no-destructive method, in a number of carbon some adsorbents and non-conventional carbon materials developed in Romania, as are: intercalated composites, nano-composites and vitreous carbon. In addition to previous studies, corresponding set of samples were examined, with special emphasis on developing of the texture during carbonization and activation. The activated carbon microstructure reveals some interesting aspects concerning the thermal processes as evolution, efficiency and pore development. In the activated carbon the adsorption surface development through a highly porous system, depends on the type of petrographical components, raw material grain size and pyrogenation-activation parameters. In the non-conventional carbon materials manufacturing, the physical-chemical characteristics depend on the type of petrographic composition of the raw materials and processing conditions, with influence on the products performances. The paper reveals that microscopically evaluation could be useful even in some domains in which only the classical physical methods seem to be efficient.

INTRODUCTION

The present paper includes some aspects of petrographic application in the field of activated carbons and the products of advanced technologies, as: intercalated composites, nano-composites and, vitreous carbon, as non-conventional carbon materials.

The development of the purification of coke oven gas, the obtaining of high quality pitches, high grade carbon products and precursors for activated carbon manufacturing required, since the very beginning, a huge work of research in laboratory and on the industrial platforms, which led to the development of this discipline in Romania.[1,2] The researchers approached the most different problems of carbon precursors and adsorbents manufacturing, during the technological process of pyrogenation-activation from xylite and brown coals,[3-5] as well as new types of carbon materials with an increased added value on the carbon materials market. [6] Some works have been undertaken to provide information by means of petrographic data on new carbon adsorbents [7-13] and in the recent years, of non-conventional carbon materials developed during original PhD theses. [14-18] The previous presentation of the petrographic studies applied to classical carbons [19] is completed in this review-paper with more recently researches, thoroughly on the carbon materials.

In addition to former studies regarding the xylite activated carbon,[5] a corresponding set of new samples of wooden wastes activated carbons were examined, with special emphasis on developing of the texture during carbonization and activation. Recent results on new carbon materials were correlated with quality of the end products giving the possibility of finding new ways to improve technological manufacturing processes.

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CHARACTERIZATION OF THE ACTIVATED CARBON PRODUCED FROM RECYCLED MATERIALS

An interesting and successfully petrographic study refers to the activated carbon produced in Roumania, for the aim of air and water purification by the use of recycled waste materials. The raw material is represented by vegetal wastes of wooden origin, especially structured as cellulose. Some vegetal wastes proposed to be used are different hard & soft lignocellulosic materials from the industry and agriculture, not used in other purposes.

By carbonization (550-650^{o}C) and physical activation (950-1000^{o}C) they develop an extended pore texture that represents a large adsorption surface area, possible to be controlled. During pyrogenation process the chars' structures display the relation between the lignocellulosic type of the wastes and the activated carbon textures. The new products prove a porous structure developed mainly of micropores giving good adsorptive properties. The petrographic research have monitoried the steps of manufacturing processes as being very important for the final textural structure of the activated carbon.

In terms of quantitative petrographic composition of the activated carbons used for the purification purposes, polished sections of seventeen average samples were investigated having nine different wooden wastes origins: particleboard PAL, wood, corn, soybean hulls, fruit kernels, cotton and a commercial sample.[7-13] To evaluate the porosity size regarding degassing extent of the activated carbon, the structural types specific to the native wastes were registered on seven pore sizes (μm): <2.5; 2.5-5.0; 5.0-7.5; 7.5-10.0; 10.0-12.5; 12.5-15.0; >15.0 (Table 1 and Fig. 1).

Table 1

Activated carbon inter-grain porosity, by size, %

Raw material type	Pore size, [μm]						
	<2.5	2.5-5	5-7	7-10	10-12	12-15	>15
PAL	32.5	40.5	12.3	7.6	1.6	4.0	1.5
Wood	37.5	41.5	8.2	6.5	3.2	1.5	1.8
Nut shells	48.0	38.7	9.1	2.0	1.7	0.5	-
Plum kernels	40.8	38.5	11.7	6.5	1.5	0.2	0.8
Soybean	32.5	41.2	16.3	3.1	3.1	1.0	2.8
Corn stalk	36.7	29.2	14.1	8.3	6.1	4.8	0.8
Corn cob	28.2	31.3	10.5	10.0	9.2	6.1	4.7
Cotton	43.2	39.6	7.2	3.8	3.8	0.7	-
Commercial	36.2	42.5	14.3	3.4	2.3	1.3	-

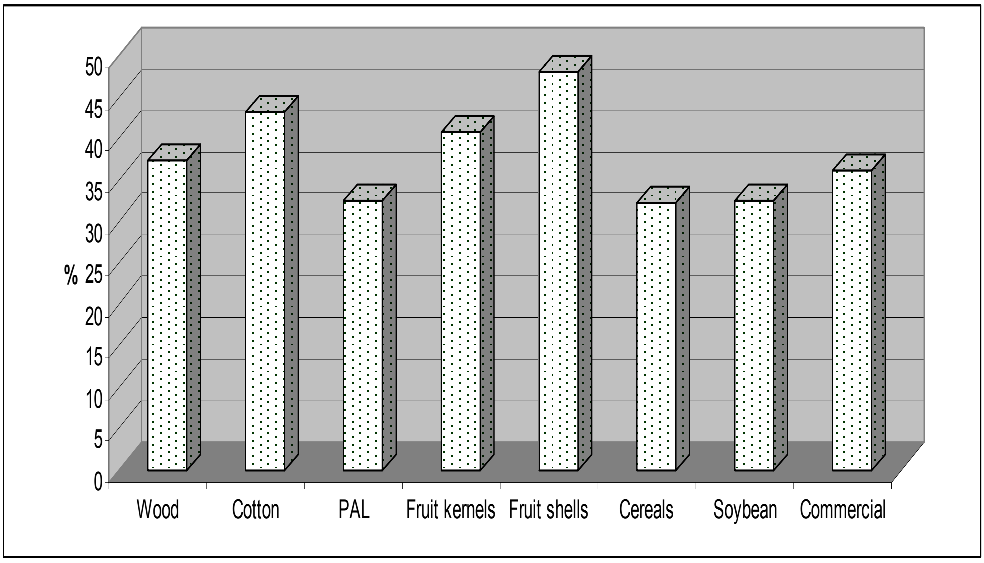

Fig. 1 – Activated carbon inter-grain porosity < 2.5 μm distribution.

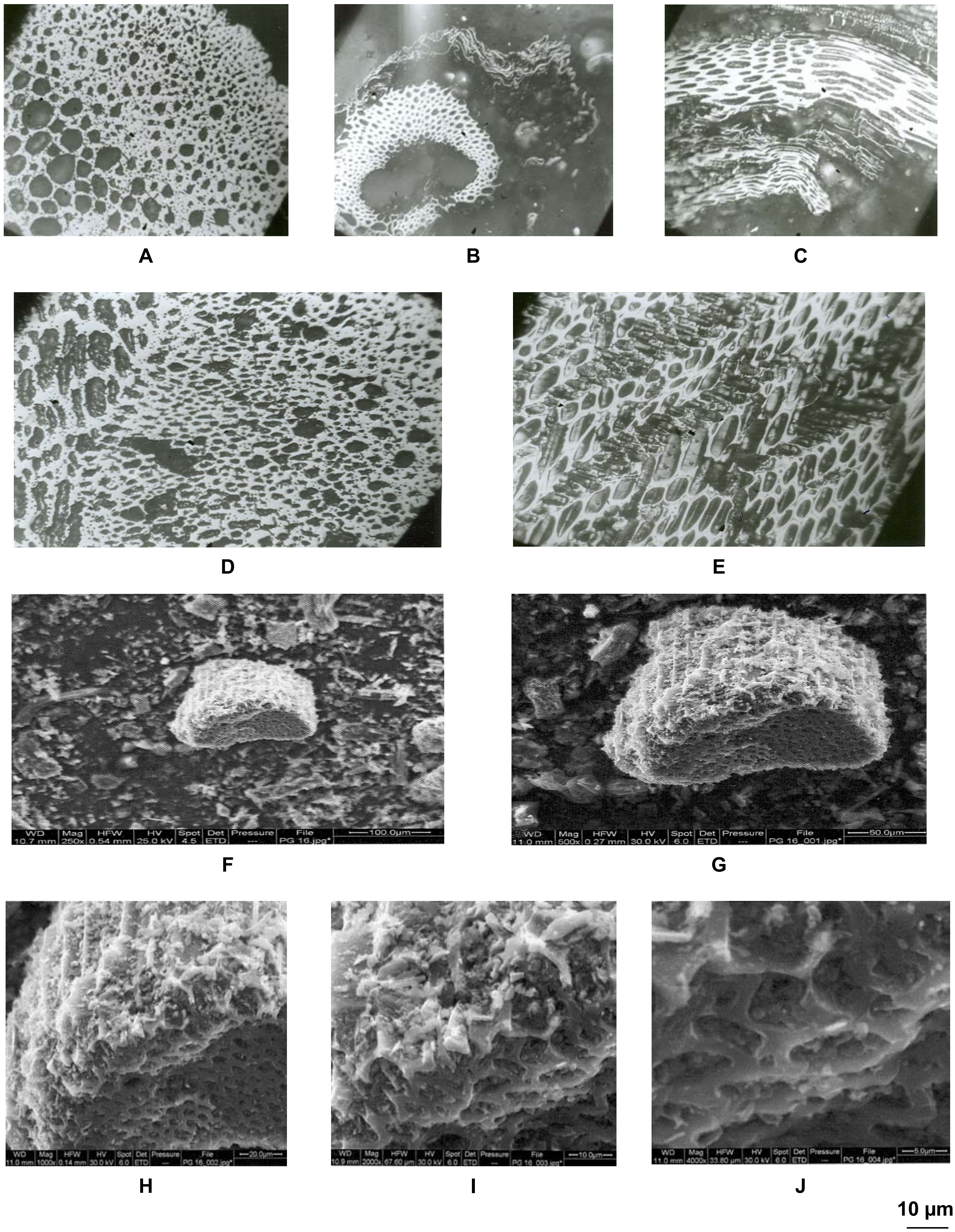

Fig. 2 – Optical (under polarized light, oil immersion, and 375 x) and SEM photomicrographs of activated carbon of different vegetal origin. (A) Wooden structure in activated fruit kernels carbon. (B) Thin pores in activated corn stalk carbon. (C) Elongated pores in activated corn stalk carbon. (D). Microstructure of mixed pores in fruit kernels activated carbon. (E). Microstructure of compact wooden structure in wood wastes activated carbon. SEM photomicrographs of the textural aspects of some corn stalk fragments, (F) 250x. (G) 500x. (H) 1000x. (I). 2000x. (J). 4000x.[6]

The structure repartition within the seven porosity categories was made using the ocular micrometer. Only particles greater than 0.2 mm, on which the inter-grain porosity could be determined, were counted as the smaller particles have usually an opened porosity, typical for the walls of very fine and fractured pores. The degassing development and the structural transformations in the stage of activation were also evaluated. The porosity distribution within the pore sizes shows that under 2.5 μm the lignocellulosic wastes ranges between 28-36% for soft materials, 32-37% for wooden, and 40-48% for hard materials, Fig. 1. Fruit kernels and shells show the finest of the majority of the pores. The photomicrographs taken on the optical microscope reveal the influence of the vegetal structure of the parent waste on the activated carbon pores Fig. 2 (A-E). An interesting contribution and completion for the petrographic study (structure and texture) appears in photo-micrographs by the use of electronic microscopy (SEM), in Fig.2 (F-J).

GRAPHITE INTERCALATED COMPOUNDS

The characterization of microstructure and texture of some graphite intercalated compounds (GIC_S) gives the possibility of a thorough understanding of physical-chemical process of intercalation. It depends of the graphite acceptance capacity for various atoms, ions and even molecules, being able to produce numerous compounds with different novelty properties required for development of advanced technologies. The GIC_S synthesis is considered to be one way of developing the functionality of carbon materials. Structural evolution stages and the final texture configuration are a consequence of the applied process parameters (temperature, reaction time etc) on the intercalation process of a carbon substrate (natural graphite).[14]

The graphite structural changes evolved during the process were microscopically revealed and analysed. Due to the carbon layers orientation, there are stacking sequence, and distance between them. Fig.3 shows two different stages in the structure organization: smaller units less orientated and partially banded (Fig.3A); better organization in expanded units, packed in sheets, without network defects (Fig.3B). The petrographic research of the pore shape and dimensions show that the progress of intercalation stage, related to the carbon layers expansion degree and the particle dimension decreasing, lead to enlarging of the surface area. That has a direct consequence on the sorption capacity of the synthesized compounds, and not only.[14,18]

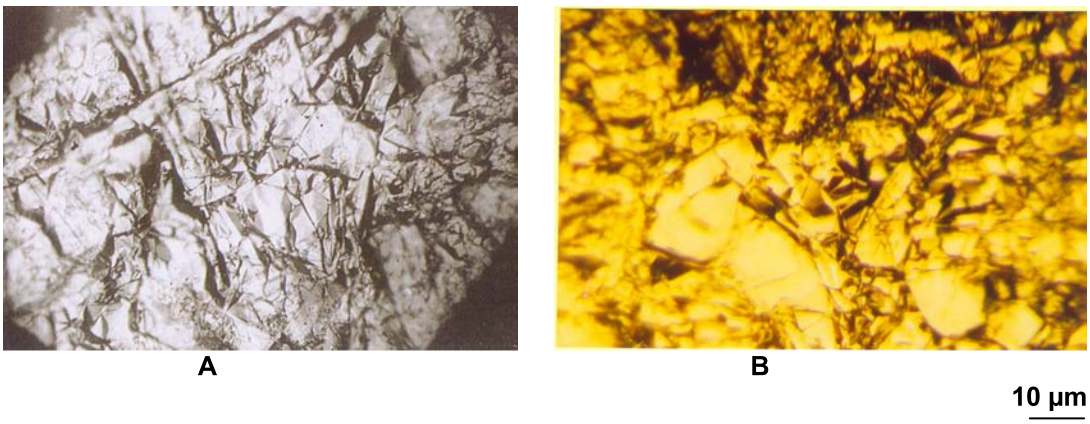

Fig. 3 – Photomicrographs of some graphite intercalated compounds, polarized light, oil immersion, nichols, 250x. (A). Smaller units less orientated and partially banded. (B). Better organization in expanded intercalated units, packed in sheets without network defects.[14]

NEW CARBON-CARBON NANOCOMPOSITES

A special attention have been carried out in order to obtain new and advanced carbon composite materials with high technical performances. These materials, in the form of carbon matrix doped with nanocarbon powder as “self assembled systems”, opened a worldwide scientific challenge. It has been studied the influence of the surface characteristics on the structural morphology, developing a multicomponent system, in which the mesophase pitch represents the C-C composite matrix and nanocarbon additives – the dispersed phase. For this study, carbopetrographic researches have been carried out using optical microscopy and "image processing analysis".[15,18] The results established the following: dispersing of the mesophase pitch units, within the temperature range of 420-450^{o}C (Fig.4A); their immediate coalescence in larger units, (Fig.4B) and anisotropic coke formation, (Fig.4C); influence of nanocarbon additives on the evolution of matrix morphology with temperature and on the isotropic/anisotropic ratio closely related to the matrix kinetic's parameters in the composite systems.

The performing of the Image Processing Analysis developed an efficient prognosis method to investigate the mesophase's evolution process. This makes possible a statistically evaluation of mesophase units on size distribution (Fig.4D).[15]

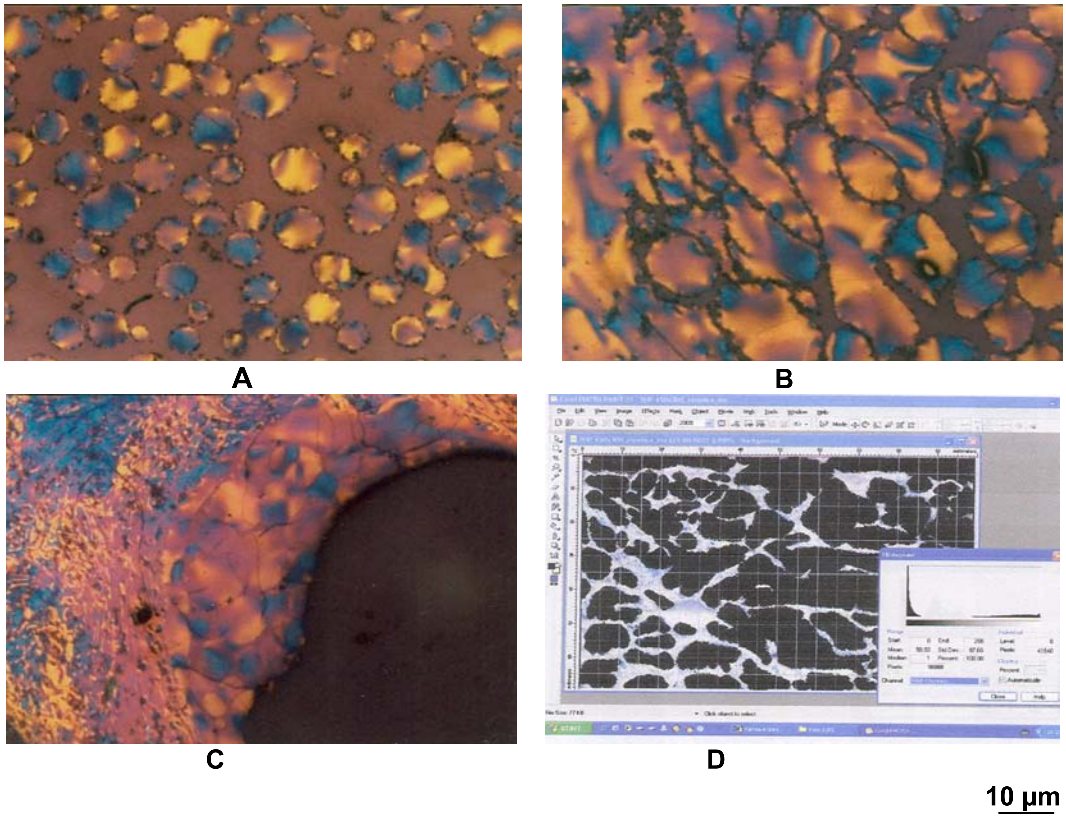

Fig. 4 – Photomicrographs of some carbon-carbon nanocomposites, polarized light, oil immersion, nichols, 250x. (A). Dispersed mesophase pitch units (B). Mesophase pitch coalescence in larger units (C). Microstructure aspect of anisotropic coke formation (D). Statistically evaluation of mesophase units on size distribution.[15]

All these findings have a tremendous importance on the carbon-graphite industry which, for the first time, has got an operation theory regarding the manufacturing of graphitizated carbons.

VITREOUS CARBONS STRUCTURAL CHARACTERIZATION

This study reveals very interesting structural aspects of carbon textures formed during morphological changes determined by heat treatment. That helps to establish the critical temperature of the basic vitreous carbon structure formation. Some types of synthetic resins were utilized as raw material precursors, usually used in mould production for alloy casting. The textures of resultant chars, at temperatures between 800-1200^{o}C and up to graphitization at 2700^{o}C, were characterized also by optical microscopy.

The study provided new information about microstructure and texture of vitreous carbon, developed on pyrogeration, complementary to physical-chemical ones.[16,17] The corresponding images are presented in Fig.5A-B.

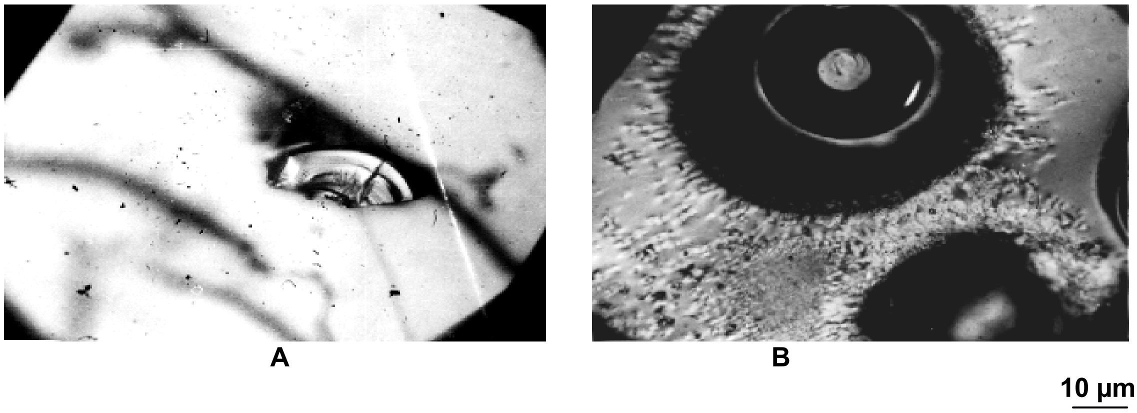

Fig. 5 – Photomicrographs of some vitreous carbon nanocomposites, polarized light, oil immersion, nichols, 250x. (A). Isotropic matrix of vitreous carbon with pyrocarbon buds having different degrees of structural orientation (B). Needle textures of vitreous graphitizated carbon samples with different size and anisotropic intensity.[16]

Vitreous carbon obtained on high pyrogenation temperatures shows isotropic matrix, in which pyrocarbon buds, with different degrees of structural orientation, occur (Fig.5A). In graphitizated samples appear needle textures of different size and anisotropic intensity (Fig.5B).[16-18]

Except the chemical-technical analyses necessary for representative samples selection, the most of the investigations have been carried out on carbon samples petrographic characteristics. For the quantitative and qualitative determinations of different types of carbon materials, have been used average sample prepared as granular blocks. The method of preparing the samples and determining microstructure characteristics and composition followed international standards.

The extended petrographic study for all carbon samples was carried out using a binocular optical microscope type MC1, under reflected natural light (RL), glycerine immersion and 125-375x magnification. Pyrogenated samples have been studied under polarized light (PL), with partial or total crossed nichols. For every block there were considered minimum 500 points. The photomicrographs were taken with an Exakta-Varex camera. The intermediate and final carbon samples were collected from the corresponding laboratory research trials.

Determination of petrographic composition for activated carbon represents a small investigated field worldwide, which is relevant for the original character of this study. The activated carbons porous structure depends to the greater extent on the type of the raw material, grain size, carbonization and activation temperature and the reaction time during both processes. An important role is played by the porosity development, as well as by the relationship between the particles microstructure and the type and dimensions of their microporosity versus the surface and adsorption capacities.

Microstructure and texture characterization of some intercalated graphite compounds (GIC_S) gives the possibility of a through understanding of physical-chemical process of intercalation.

The investigation on carbon-carbon nanocomposites reveals the development of mesophase pitch units, within the temperature range, their coalescence and anisotropic coke formation as well as the influence of nanocarbon additives on the evolution of matrix morphology with temperature and on the isotropic/anisotropic ratio closely related to the matrix kinetic's parameters in the composite systems.

The carbopetrographic study gives qualitative information of carbon textures formed during morphological changes determined by heat treatment by establishing the critical temperature of the basic vitreous carbon structure formation.

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