



Coal-liquid based upgraded carbon materials for energy storage **(SUPERCOAL)**

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Coal-liquid based upgraded carbon materials for energy storage (SUPERCOAL)

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SUPERCOAL

Research Fund for Coal and Steel

Coal-liquid based upgraded carbon materials for energy storage ***(SUPERCOAL)***

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Final Report

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FINAL SUMMARY

WP0. COORDINATION ACTIVITIES (INCAR-CSIC)

During the development of the whole project different coordination activities were carried out to cover the Commission requirements. They were mainly focused on the development of a webpage to publicize the project, the organization of periodic meetings between the partners to share relevant information/results, the elaboration of the different reports and their report to the Commission in the framework of different TGC2 meetings.

WP1. PREPARATION OF PITCH-LIKE PRODUCTS FROM COAL-DERIVED LIQUIDS AND COKES/GRAPHITES (IQNSA / UPB / CTRom)

Task 1.1 Polymerization of anthracene oil (IQNSA / UPB / CTRom)

A process for the manufacture of carbon precursors by means of the oxidative thermal treatment of anthracene oil has been put into operation on a semi-industrial scale (5 kg h⁻¹) by IQNSA

The manufacturing process is highly flexible and allows the manufacture of carbon precursors in the entire range of optical textures from needle to isotropic cokes and can even be stopped at the appropriate crystallographic level for each application.

In contrast, two types of pitch have been studied in depth:

- Type A: Precursor of highly oriented coke structure with a needle and flow domains optical texture
- Type B: Precursor of coke with a fine mosaics optical texture

To produce these types of pitches, different operating conditions were required.

For type A the most convenient temperature was around 350 °C. At this temperature the reactivity of AO with air was high and it was needed to minimize the residence time so that conversion did not exceed 30 %.

At higher conversion rates the formed pitch reacted again increasing the molecular weight of pitch components, which was not desired as it makes more difficult obtaining a highly fluid system capable of forming highly oriented crystalline textures during the subsequent carbonization.

Treatments at 375-380 °C for 3-4 h of soaking time were revealed as promising treatments for improving pitch properties, specially wettability and rheology.

On the other hand, type B pitches required more moderate temperatures (around 250 °C), reaching higher conversion rates (50 %). The preparation of this type of pitches required high stirring conditions with a high share impeller during the distillation step.

UPB and CTRom elaborated the technological solutions and process principle schemes for anthracene oil polymerisation by (1) microwave heating and by (2) conventional heating. Given the high degree of novelty of the microwave technology applied to polymerization of the anthracene oil, UPB and CTRom developed a small-scale experimental laboratory module, to study the process in a preliminary phase.

Data of the unconventional/conventional heating laboratory equipment were presented, as: profile and capacity, equipment technological description, process flow sheets, main constructive requests for technological assembling (design principle scheme, working conditions, constructive and functional specificity of equipments). Elaboration of technological description and design of execution details for realisation of two small scale equipment was carried out: (I) Equipment for unconventional oxidative treatment of anthracene oil assisted by microwave heating in a discontinuous small-scale reactor which was used for preliminary studies to achieve the demonstrator. (II) Equipment for conventional heating of carbon precursors (at low and high temperature) (within Task 3.1). The design details (21 drawings) for construction of conventional heating equipment were elaborated to correspond in terms of functional working conditions required by the regulation in force and data published in the literature. The suggested process flow sheet and technology on stages and operations were presented.

Two documents were additionally provided by UPB related to microwave heating: Fundamentals and application and Main results related to activated carbons manufacturing (both enclosed in the *First Annual Report*).

After running the lab scale tests (phase I single mode applicator) within the unconventional discontinuous small-scale reactor (AO amount varying between 7 and 32 g), CTRom started the construction of a preliminary equipment having 1 microwave generator and after that, 3 microwave generators (phase II multimode applicator). The semi-pilot equipment was used to obtain the

preliminary information necessary for scaling-up the process. Conclusion drawn from experiments in phase I was confirmed by the phase II of AO oxidative microwave heating. During 2017, CTRom and UPB carried out the targeted experiments to use AO amount varying between 200-1400 g and obtain suitable AO representative pitch (around 150 g).

For comparative purposes the experiments were also carried out by using conventional heating (*First Annual Report, Mid-Term Report*). Energy consumption studies during conventional and microwave heating were evaluated and enclosed in the *Second Annual Report*. It was preliminary proven a considerable decrease of microwave energy consumption by 62.6 % compared to the conventional heating.

According to Task 1.1 during 2017-2018 CTRom scaled-up the process and designed and manufactured a pilot scale equipment of larger capacity (5000 mL), for polymerization of AO using an innovative technique based on direct microwave heating (enclosed in *Deliverable 3.2: Report on the ACs standard characteristics of present Final Report*).

Conclusions drawn from experiments in pilot phase were confirmed by the oxidative microwave heating of AO. It was found that a temperature up to 335 °C, a slow gradient (2-5 °C min⁻¹) and oxidation times by 2-3 hours, favours the production of characteristic hard pitches with Mettler softening points over 90 °C, suitable to be used as precursors for graphene materials.

Task 1.2 Preparation of QI-free coal tars (IQNSA)

An alternative method for the manufacture of carbonaceous precursors from tar is the physical removal of their impurities (ashes and carry-over).

To this end, a semi-industrial scale process has been established for its elimination through anti-solvent technology, using a paraffinic solvent for its separation.

By using this technology, the solid particles containing tar as impurities are sedimented and are easily separable by density.

The method has been contrasted in comparison with a filtration yielding equivalent results. Filtration is a process that cannot be implemented industrially due to its high operational costs and low yields.

Task 1.3 Characterization of raw materials and pitch-like products (IQNSA / UPB)

Anthracene oil and coal tars have been characterized according to standard industrial test methods, i.e. distillation profile, insoluble content in toluene and Quinoline and ashes. Pitches were also characterized by softening point, elemental analysis and the optical texture of the resultant cokes after carbonization.

The characterization of the two (2) initial samples of AO and IP (isotropic pitch) provided by IQNSA was carried out by the Romanian partners by standard physical-chemical procedures applied to coal derived products. The characterization of the samples was carried out by standard procedures (proximate analysis, softening point, solubility parameters TI, QI, etc.).

The results showed that AO is a high-grade raw material, which characteristics fall in the limit of values for such type of products. The information obtained in this task was used to assess the effect of the composition and properties of the coal-derived liquids on their conversion to isotropic/mesophase pitches and coke/graphite precursors with the desired characteristics. High purity carbon precursor, given by the lack of quinoline insoluble, assured structure continuity favouring the formation of anisotropic carbon, properties that were able to produce active materials with determined characteristics of morphology, microstructure, surface chemistry and electrical conductivity targeted in our project.

Task 1.4 Preparation and characterization of cokes and graphites (IQNSA / UPB / CTRom)

IQNSA has scaled and put into operation a carbonization furnace complying with ATEX industrial safety standards. The oven with a capacity of 5 kg per batch, can operate under vacuum and pressure conditions and up to a temperature of 1100 °C.

UPB and CTRom have obtained low temperature cokes from pitch-like products obtained by AO oxidative polymerization in microwave field. This represented a novel approach to test the ability of a carbon material precursor as "absorbing material" to enhance the rate of pitch pyrolysis in the microwave field. Two experimental equipments were used to obtain the pitch cokes: a conventional heating one and a semi-pilot preliminary equipment heated by microwaves, both created by CTRom. Different experimental parameters were tested to afford the best conditions. Because temperature measurement was a challenging aspect under microwaves, experiments were carried out using an infrared temperature sensor. A comparison of the data obtained from temperature-time together with the yields and analysis of products of conventional heating (UPB) and microwave pyrolysis (CTRom) were considered (*First Annual Report, Mid-Term Report and Second Annual Report*).

For obtaining semi - coke, different temperatures were selected (600, 650 and 700 °C) in order to compare the final results with those obtained by conventional heating for the same temperatures. Beside these, different temperatures were selected (500, 680, 1000 °C) in order to observe modifications in microwave field. The soaking time was varied between 0.5-1 h. The heating time in the microwave was four times lesser than conventional heating knowing that the thermal gradient for conventional was 2 °C min⁻¹.

Special emphasis was given to the differences found in the final products by conventional and unconventional treatments characterizing the cokes by standard procedures (proximate analysis, real density, apparent density, porosity) as well as by optical microscopy.

40 samples of low temperature pitch cokes were characterized in 2016-2018 (proximate analysis, real density, apparent density, porosity) following the Romanian standards used in UPB laboratory (*Mid-Term Report*).

In the final phase of the project CTRom/UPB produced 6 coke samples which were supplied, as precursor for the synthesis of graphene materials to INCAR.

A comparison of the data obtained from temperature-time together with the yields and analysis of products (UPB) of microwave pyrolysis (CTRom) were considered and enclosed in the *Deliverable 3.2 Report on the ACs standard characteristics* of present *Final Report*. According with the objectives of the task, green cokes at 450 and 480 °C under nitrogen flow, were produced (in terms of microwave heating by using new laboratory equipment specially designed for this purpose). Coke samples pyrolyzed at 450-480 °C showed an increased well-developed optical texture. This seems to indicate that mesophase spherules had enough time to nucleate, grow, and to associate as chains of mesophase spherules that coalesce and grow in highly developed optical textures

WP2. PREPARATION OF POLYMERIZED ISOTROPIC AND MESOPHASE PITCHES (IQNSA / UPB / CTRom)

Task 2.1 Preparation of polymerized isotropic pitches (IQNSA)

All samples obtained from the "Reaction Products", were distilled by IQNSA to obtain the corresponding pitches in order to increase the yield in the eventual coking process. This distillation was carried out in the same Pilot Plant under vacuum conditions (10 mbar).

Due to the similarities of the actions carried out within this task and the next one, the most relevant actions of both of them have been presented in Task 2.2.

All isotropic pitches were manufactured following the same process, i.e. selection of the appropriate precursor (coal-tar without QI or anthracene oil), for the anthracene oil followed by an oxidative thermal polymerization, and additional distillation until reaching the desired softening point.

In this sense, for the isotropic pitch to can be used for the manufacture of carbonaceous materials, the softening point should be higher than 250 °C so that it can be easily thermostated generally using air.

The distillation has to be carried out at the lowest possible temperature and with maximum vacuum to inhibit the formation of mesophase. Adequate stirring, and even vigorous, favors this aspect.

Task 2.2 Preparation of mesophase pitches (IQNSA / UPB / CTRom)

From the beginning of the project, IQNSA was aware of the difficulty of carrying out the manufacture of a mesophase pitch according to the current market standards since the softening point increased faster than the mesophase formation. For this purpose, a non-dehydrogenative polymerization process or a catalytic hydrogenation step had to be carried out. Both processes were beyond the scope of the project and the experience and knowledge of IQNSA.

In this sense and given that the objective of these precursors was the manufacture of activated carbons where the softening did not matter, instead of proper mesophase, a coke as green as possible was made for that purpose; that it was totally anisotropic but without yet having the structural and crystalline perfection of a coke. In this way the material would look more like the mesophase in itself than a coke. For this reason, in this report we use the terms green coke or mesophase pitch as a synonymous.

After obtaining a product with an adjusted softening point (coke precursor) the following steps were:

- Intermediate thermal treatment at temperatures around 400-650 °C to produce mesophase / green cokes
- For a mesophase pitch it is important that this preliminary step was performed under nitrogen pressure and with a smooth stirring with the right impeller (confidential information), followed by sudden expansion at the end of the thermal treatment followed

by a soaking time of at least half an hour to eight according with temperature. Temperature should not be higher than 475 °C.

- For cokes, this first step should be also carried out under nitrogen pressure to increase the global yield and temperature need to be 650 °C to ensure thermosetting of the green coke. Sudden expansion is not necessary.
- For fine mosaics like cokes stirring with the right speed and impeller (confidential information) until the material is almost thermoset is critical
- For needle or large domains like cokes stirring is not as critical but can favor homogeneity. If stirring is selected, it should be very smooth and with the right impeller like the mesophase pitch one.

Additional thermal treatment at temperatures between 1000-1100 °C at atmospheric pressure is required to obtain cokes.

The raw material used in Task 2.2 was a pitch sample obtained through oxidative polymerization in a microwave field of AO distillation residue. The conditions used for the preparation of the mesophase pitch were: heating rate of 11-12 °C min⁻¹ up to a final temperature of 480 °C and soaking time of 1-2 min. Due to the special conditions of heat generated by the microwave field, the samples for the microscopical characterization were taken from the edge and centre/heart of the semicoke button. Through petrographic analysis was identified the mesophase formation from the isotropic aromatic parent AO pitch to an anisotropic solid texture (nucleation, coalescing, mesophase coalescing final stage), which revealed the novelty of our research (*Mid-Term Report*).

The presence of coalesced regions appeared related to the absence of primary QI in this type of pitch, because that AO is obtained as a distillate. Type of mesophase not differed from the well-known mesophase of coal-tar pitch. It was observed that the spherules had not enough time to nucleate and grow, but to associate as chains of mesophase spherules. Mesophase appeared only in samples taken from the core of coke sample. At the edge of sample, no mesophase spherulites appeared.

This experiment was a proof of concept concerning the microwave technology heating which cause heating to the inside of the sample and not by classic heat transfer from outside to inside. High heating rate may cause the mesophase association prior to mesophase growth that happens when heating with low gradients.

Task 2.3 Characterization of carbon materials precursors (IQNSA / UPB)

All the precursor and raw material for the specific target carbon material for the project were submitted to the rest of the partners and characterized from both sides INCAR-CSIC and IQNSA.

From the point of view of IQNSA, the greatest characterization effort has been made by polarized light microscopy. This technique allows to directly observing the formation of graphitic structures from its amorphous / isotropic state to coke / graphite in all its stages. Each of these stages has been relevant to observe the level of cleanliness in the removal of impurities from the tar, the preparation of mesophase pitches to be able to stop the carbonization just after the complete coalescence of the mesophase, as well as to see the formation of the crystal-like textures in the form of a needle, domains and mosaics.

The characterization of the different polymerized isotropic pitches obtained was carried out by standard procedures (proximate analysis, solubility parameters, softening point). The results have been detailed in the *Mid-Term, Second Annual report and Final Report* which summarize the most representative pitches that were subsequently used by INCAR-CSIC as precursors for the synthesis of ACs and graphene materials. The formation of anisotropic mesophase pitches from the isotropic phase during microwave and conventional heating and the structural organization before and after solidification to low temperature coke was identified. The optical texture was defined by the size, shape, and orientation of the different mesophase spheres corresponding to different pyrogenation stages. The morphological differences between the sample precursors type, the influence of heating rate within the temperature interval (which will ensure a certain range of physical properties of the products) was also evaluated.

WP3. SYNTHESIS AND CHARACTERIZATION OF ACTIVATED CARBONS (ACs) (UPB / CTRom / TUWRO)

Task 3.1 Influence of the selection of carbon precursors (polymerized isotropic/mesophase pitches and low temperature cokes) and activation procedures on the activated carbons characteristics (UPB / CTRom)

The work carried out was mainly aimed at defining the conditions of AO processing as precursor of carbon materials. Consequently, they gave rise to documentation, in the present state of knowledge, for defining the experimental frame for the subsequent applications, in terms of using microwave heat technology for the studied processes. Starting from the very first stage of the

project, the realization of equipment for classical/conventional heat treatment, specific for the requirements of the foreseen activities, was justified by the following reasons: (i) High degree of novelty of microwave heating technology applied to the treatment of coal liquid-based carbon precursors. (ii) Choosing of one single functional model, where both thermal processes can be achieved (pyrogenation at temperatures of 480 - 700, 850 and 1000 °C as well as activation at 1000 °C).

The technical documentation - technological solutions - and the process details designs SCP 001

(16 drawings) and SCP 004 (5 drawings) were elaborated and were enclosed in the *Mid-Term Report*.

As stated, the temperature to obtain the carbon precursor influences the adsorption of the AC capacity expressed by the iodine value and S_{BET} . Both parameters decrease when increasing temperature from that of the green coke (480-500 °C) to the high coke temperature (over 900 °C). Preliminary chemical activation tests using microwave heating of AO and pitch cokes showed that the iodine value and S_{BET} increase as the soaking time at max. temperature increasing from 10, 20 and 30 minutes.

The UPB laboratory procedure was presented in detail in *Deliverable D3.1: Report on the Activation technology performance* enclosed in the *Mid-Term Report*. The details of operating parameters (method, parameters investigated, simulation of electromagnetic field), and characteristics of the activated carbons obtained in the pilot stage appear in *Deliverable 3.2: Report on the ACs standard characteristics* of present *Final Report*.

The samples obtained during the experiments of chemical activation by microwave heating were characterized by UPB and were sent to INCAR for complex characterization.

In parallel, INCAR-CSIC synthesized different ACs by chemical activation and the subsequent conventional heating of both, green cokes provided by IQNSA and a green coke derived from a microwave pitch. The aim of this research was to compare these ACs with those obtained by UPB following other activation methods and/or microwave heating.

Task 3.2 Preliminary characterization of the activated carbons synthesized (UPB)

Characteristics of the activated carbons were detailed in *Deliverable D3.1: Report on the Activation technology performance* enclosed in the *Mid-Term Report*.

According to the results obtained in the preliminary phase of the experiments, the ratio between green coke:KOH was increased from 1:3 to 1:4 to obtain a higher surface area of the carbon precursor. The reason is that the interaction of KOH is more effective in coke of 450 °C, less carbonized compared to that of 480 °C, which has an increased carbon structural organization and thus, is more resistant to attack by KOH. Chemical activation at 700 °C produces typical changes for this type of material: extension of pores with weight loss increasing starting with the ultra-microporosity, which is gradually transformed in micropores. Chemical activation using microwave heating of AO pitch green cokes show that the S_{BET} does not increase as the soak time at max. temperature increased from 1 to 2 hours. This allowed in the final stage of the experiments an increase in the adsorption capacity of the resulting AC according to the iodine value and S_{BET} . Green coke (of 450 °C) is suitable for chemical activation obtaining a iodine value over 1220 mg g⁻¹ and a surface area, S_{BET} , over 2200 m² g⁻¹. From the porosimetric analysis for all samples analyzed an average pore radius between 14-20 Å results which shows large volume of AC micropores.

The optical microstructural studies on the activated carbon, revealed the different appearance of textures in chemical activation. Depending on carbon type (green coke) they reveal the decreasing of porosity up to a certain limit. After that, the progressive weight loss of carbon substance takes place which lead to the pores enlargement and the decreasing of the adsorption surface (details are presented in *D 3.2. Report on the ACs standard characteristics*, enclosed in present *Final report*.

Regarding the ACs synthesized by INCAR-CSIC with comparative purposes, it was observed that the AC obtained, following a conventional route but starting from a microwave derived precursor, showed better characteristics than those previously obtained from conventional precursors. This result corroborates microwave technology as a novel route to obtain suitable carbon precursors.

Task 3.3 Activated carbons with different oxygen functional groups distribution (TUWRO)

The ACs provided by INCAR were subjected to different oxidative treatments to introduce the oxygen functional groups on the carbon surface. Several approaches were applied such as wet oxidation using a mixture of nitric and sulfuric acids, ammonium persulfate, oxidation with air and electrochemical oxidation. The goal was to increase the oxygen content as high as possible maintaining the specific surface area of the initial AC to the highest extent. The oxygen content in the ACs obtained by different oxidative treatments varied between 6.4 and 29.7 wt. % and was higher compared with the pristine ACs. A decrease in the BET surface area was in the range of

1.834.4 % due to oxidation. Air oxidation was revealed to be the most promising method of AC treatment to obtain the AC with enhanced oxygen content and only slightly lower porosity development than that of the pristine AC. The influence of temperature and time of oxidative treatment with air on the oxygen content and porous structure of the modified AC was determined. The oxygen functional groups distribution is related to the method applied and processing parameters of oxidative treatment.

Task 3.4 Activated carbons with different N-containing functional groups distribution (TUWRO)

The ACs provided by INCAR were subjected to different treatments to introduce the nitrogen functional groups on the carbon surface. For this purpose, different approaches were applied, including thermal treatment of AC in ammonia, hydrothermal treatment in the presence of ammonia and reaction with urea. Temperature was the main variable of the studied processes. The content of nitrogen in N-doped ACs ranged from 2.4 to 5.5 wt. %. Enrichment in nitrogen was followed by reduction of oxygen content. Depending on the method used, a decrease of BET surface area was in the range of 2.7- 44.4 %. Heat treatment of AC under an ammonia flow at 450 °C appeared to be the best method in order to introduce a high amount of nitrogen (up to 3.1 wt. %) into the carbon structure with a minimal decrease in the porosity development. The nitrogen functional groups distribution is determined by the applied N-doping method and its processing parameters.

WP4. SYNTHESIS AND CHARACTERIZATION OF GRAPHENE (G) (INCAR-CSIC / IQNSA)

Task 4.1 Graphene from coal-liquid based graphites by the chemical route (INCAR-CSIC)

Several graphene materials were obtained by following the chemical route (a modified Hummers method) starting from the different graphites produced inside the project. For the first time, graphenes from microwave derived precursors were obtained. After their preliminary characterization, it was demonstrated that the microwave technology represents an alternative route for obtaining graphene materials with similar or even better characteristics to the conventional ones mainly in terms of morphology (completely exfoliated materials), chemical composition (oxygen content) and textural properties (specific surface area).

Task 4.2 Graphene from direct exfoliation of coal-liquid based graphites by using supercritical fluids (IQNSA)

IQNSA has put into operation two alternative methods to the Hummers one for the graphite exfoliation in the manufacture of graphene. Both methods can be considered sustainable due they do not generate toxic waste, scalable because they have been put into operation continuously and close to a capacity what could be appropriate scaling at the industrial level for the current market volume of these materials, and economic once evaluated the energy costs, reagents and personnel required have been made.

The path of obtaining graphene by the oxidation route with hydrogen peroxide under supercritical water conditions also offers the possibility of obtaining graphene oxide (a product also useful for different applications) with the peculiarity of being able to be thermally reduced by hydrothermal reduction in situ within the reaction / expansion stage simply by coupling an intermediate reservoir between the reactor and the expansion tower. The process also offers the possibility to obtain exfoliated materials directly from coke.

It has been demonstrated that the process requires additional optimization as they produce heterogeneous samples; more important when graphite is used as raw material maybe because its lower reactivity. Although these methods do not currently offer the quality of graphene offered by the Hummers method, it can be used in various applications that currently have a high relative consumption.

Regarding the materials that have been obtained through oxidative exfoliation in supercritical water regime, the most important ones are the Graphene Quantum Dots. It is important to remark that, when compared to those currently offered in the market, those produced under the present project maintain their fluorescence over time. In any case, they require optimization in order to enhance their intensity.

Following the same operative procedure, standard graphite gives higher dispersion and heterogeneity. The process has also been carried out with coal tar pitch coke (without graphitization) thus showing the best results.

WP5. PREPARATION OF COMPOSITES ACTIVATED CARBON/GRAPHENE (AC/G) (INCAR-CSIC / UPB / CTRom)

Task 5.1 Synthesis of composite materials activated carbon/graphene (INCAR-CSIC / UPB / CTRom)

Different strategies were followed to obtain composites AC/G with suitable properties (mainly in terms of specific surface area, oxygen content and electrical conductivity) to be used as electrodes in the electrochemical devices investigated (SCs and hybrid systems). The first one was the combination (by simple physical mixture) of different ACs and G. Another route was the direct synthesis of the composite starting from an AC and a G precursor (graphene oxide water suspension). In this last case, the resulting suspension was treated following two different procedures: solvent removal/thermal treatment or direct hydrothermal treatment of the suspension.

Task 5.2 Preliminary characterization of the composite materials (INCAR-CSIC / UPB)

The resultant materials from the different procedures above mentioned were preliminary characterized by elemental analysis, SEM and N_2 adsorption at $-196.1\text{ }^\circ\text{C}$. Mainly those from the second route exhibited an interesting morphology consisting on AC particles wrapped by graphene layers and presented lower specific surface areas when comparing to the starting AC selected thus ensuring an intimate contact between the two individual components. Moreover, different oxygen contents were measured depending on the procedure followed (solvent removal/thermal treatment or direct hydrothermal treatment) thus offering the possibility of studying the influence of the different characteristics observed on their electrochemical performance in the different devices evaluated.

WP6. ENERGY STORAGE SYSTEMS: SUPERCAPACITORS (SCs) AND HYBRID SYSTEMS (TUWRO / INCAR-CSIC)

Task 6.1 Testing of active electrode materials in supercapacitors operating in aqueous electrolyte (TUWRO)

All activated carbons tested in this task show extremely high specific capacity (up to 335 F g^{-1} at 0.2 A g^{-1} in 6M KOH). Air and wet oxidation of ACs lead to an increase in the content of surface oxygen groups which are responsible for the pseudocapacitance effect. However, the overall gravimetric capacitance of the oxidized ACs is not enhanced but is comparable or lower than that of the pristine ACs, because a decrease in the specific surface area occurs due to oxidative treatment. The same finding was revealed for N-doped ACs. However, the introduction of oxygen and nitrogen groups on the AC surface enhances the specific surface capacitance which reflects the contribution of pseudocapacitance in the overall gravimetric capacitance. A linear correlation between the specific surface capacitance and the heteroatoms content proves that the oxygen and nitrogen groups are responsible for the pseudocapacitance effect to the comparable extent. Electrochemical testing of the pristine and modified ACs as active electrode materials revealed that the overpotential of water decomposition is slightly higher in $0.5\text{ M Na}_2\text{SO}_4$ than 6M KOH as an electrolyte. The optimal asymmetric capacitor is built of SC-AC-10-300/0.5 as the positive electrode and SC-AC-11 as the negative electrode (at 1.4 mass ratio), which is able to work stable up to 1.3 V in $0.5\text{ M Na}_2\text{SO}_4$. The device is characterized by good electrochemical performance, showing an excellent stability after 10000 cycles at 2 A g^{-1} , a specific capacity of 32 F g^{-1} and an energy density of 7.5 Wh kg^{-1} .

Task 6.2 Testing of active electrode materials in hybrid energy storage systems operating in aqueous redox electrolytes (INCAR-CSIC)

The main goal of this task was the evaluation of the different materials synthesized inside the project (ACs, Gs and composite materials AC/G) as suitable electrodes in hybrid energy storage systems. In these devices one of the two electrodes acts as a battery-type electrode (supporting the development of a faradaic reaction) while the other one act as a capacitor-type electrode (contributing to the energy storage through the formation of the electrical double layer). Bearing this in mind the active electrode materials are required to exhibit mainly a proper electrical conductivity and suitable morphological/textural properties, respectively. In this context, and a preliminary step in the development of hybrid energy storage devices operating in aqueous redox electrolytes, a screening of the electrochemical performance of the materials obtained was carried out.

Activated carbons (ACs) from conventional (green cokes) and microwave derived precursors (a green coke obtained by conventional heating from a microwave derived pitch) were tested as capacitor-type electrodes in symmetric devices (same active material in the two electrodes of the experimental set up) operating in acidic media. The results obtained, in terms of specific capacitance values at increased current densities, presented the AC from the microwave derived precursor as a suitable electrode material, even better than the ACs from the conventional technology. The obtained results were clearly related to the main characteristics of the ACs, i.e the specific surface area (S_{BET}) determined by N_2 adsorption at $-196.1\text{ }^\circ\text{C}$ and the oxygen content measured by elemental analysis.

Graphene materials (Gs) from both, conventional and microwave derived precursors were tested to be used as battery type electrodes in the hybrid devices. Thus, also symmetric devices in acidic media were firstly evaluated. The comparative of the results obtained regarding the evolution of

the specific capacitance values (F g^{-1}) and the energy density (Wh Kg^{-1}) of the systems at increased current densities applied showed that the Gs from the microwave derived precursors exhibited an electrochemical performance similar to that of the conventional ones. This represents a significant step forward as the new microwave technology, with lower time and electric energy consumptions for the preparation of the carbon precursors, results in graphene materials with similar properties than those obtained from the conventional precursors.

Following with the screening of the materials also the composites AC/G were tested in symmetric devices. It was important to remark that these materials were firstly thought as 3D networks where the graphene layers could interconnect the AC particles thus increasing the electrical conductivity of the whole material without a significant decrease in the textural properties of the later. The evaluation of the specific capacitance values, however, showed a significant decrease in C when comparing with the corresponding AC symmetric device as a result of the intimate contact between the G layers and the AC particles. Even though this decreased value, the rate performance of the device was significantly improved this was in agreement with an enhanced electrical conductivity. As a result the AC/C electrodes presented a better behavior as battery-type electrodes.

As a last step, the better battery and capacitor-type electrodes were set up in asymmetric/hybrid devices. First, the asymmetric devices were evaluated in the supporting electrolyte to achieve reference values of their electrochemical performance when combining the different materials (ACs, Gs and composites AC/G). Subsequently, the evaluation of real asymmetric/hybrid devices were carried out after introducing a Nafion membrane to separate the two half-cells (as two different electrolytes were used in both: supporting electrolyte/ solution based in vanadium ions). The C and E values of the devices were significantly improved because of the hybrid mechanism of energy storage thus representing a significant step in the search of energy storage devices with improved energy density values.

WP7. ADVANCED CHARACTERIZATION OF THE COAL-LIQUID BASED CARBON MATERIALS (UEA)

Task 7.1 Advanced characterization of the synthesized activated carbons (ACs) (UEA)

In this task, the advanced characterization (in terms of morphology, structure and chemical composition) of the synthesized activated carbons (conventional and unconventional) has been carried out. From these characterisations, it is possible to conclude that microwave technology has the potential to produce ACs with high surface area (even higher than from conventional means) and appropriate properties to be excellent materials for electrodes in supercapacitors.

In addition, the surface chemistry of the ACs with different oxygen and nitrogen functional groups distribution developed in Tasks 3.3 and 3.4 has been also studied. All the approaches were able to incorporate the required functionalities on the surface of the ACs. However, the type of functionality is very much dependent on the modification carried out.

For the integration of oxygen, it seems that the acid treatment and the modification with concentrated ammonium persulfate promote the presence of carboxyl functionalities in higher degree than air, while the treatment with ammonium persulfate incorporates a wider range of functionalities.

Good introduction of pyridine nitrogen has been achieved by the three methods explored, particularly with ammonia and urea reactions at temperatures up to $450\text{ }^{\circ}\text{C}$. Ammonia at 400 and $450\text{ }^{\circ}\text{C}$ and, hydrothermal treatment are fairly effective introducing amides/amines or lactams. Substantial percentages of pyrrolic nitrogen have been identified on the surface of these samples treated with urea.

Task 7.2 Advanced characterization of the synthesized graphene materials (G) (UEA)

In this task, the structure, surface chemistry, morphology and composition of the graphene materials synthesised were studied and exhaustively characterised.

Materials from microwaved precursors appear to be completely exfoliated when comparing with those graphenes synthesized from AO derived precursors by conventional technology, where worm-like structures were predominant.

Graphene materials obtained by unconventional routes present a lower oxygen content than those fabricated by conventional methods. Surface area values of the unconventional samples were slightly enhanced with respect to the most promising conventional materials. All the microwaved samples reduced at $1000\text{ }^{\circ}\text{C}$ accomplished higher Csp^2 content on their surfaces than conventionally obtained graphenes and showed similar distribution of oxygenated functionalities.

These results suggest that the microwave technology can be an alternative way for the synthesis of graphene materials comparable, or even improved, to the conventional approaches.

SCIENTIFIC AND TECHNICAL DESCRIPTION OF THE RESULTS

Objectives of the project

The main objective of the project has been the development of coal liquids-based carbon materials (activated carbons, graphenes and composites) with suitable properties for their use as electrodes in electrochemical energy storage devices such as supercapacitors (SCs) and hybrid systems.

With this aim, the following points have been addressed:

- Production of optimized coal-liquids based carbon precursors by conventional and unconventional technologies.
- Study of the parameters involved in the synthesis of polymerised isotropic and mesophase pitches and an evaluation of their influence on the properties of these precursors.
- Synthesis and preliminary characterization of activated carbons (ACs) and selection of the most promising for use as electrodes in the energy storage devices under study. Evaluation of the influence of the synthesis processes on their characteristics.
- Synthesis of graphenes (Gs) by different routes: optimization of the thermal exfoliation/reduction of graphite oxides and graphene oxides and development of a new alternative based on the direct exfoliation of graphites by supercritical fluids. Preliminary characterization of the graphenes obtained.
- Design of activated carbon/graphene composites as new electrode materials.
- Investigation of the suitability of the synthesized carbon materials as electrodes in SCs and a new battery-capacitor device (hybrid system) with improved energy and power density values.
- Establishment of the relationships between the processing conditions of the coal-derived liquids and the properties of the final carbon materials by means of their advanced characterization.

Description of activities and discussion

WP0. COORDINATION ACTIVITIES (INCAR-CSIC)

During the whole project (01/07/2015 to 30/06/18) the coordination activities focused on the following points:

1. Organization of periodic meetings between the partners to share information about the developments/results of the project and define actions to be carried out in the following periods:
 - Kick-off meeting in Oviedo (Spain) organized by INCAR-CSIC (10/09/15)
 - Second meeting in Norwich (United Kingdom) organized by UEA (14/04/16)
 - Third meeting in Bucharest (Romania) organized by UPB/CTRom (13/10/16)
 - Fourth meeting in Wroclaw (Poland) organized by TUWRO (25/04/17)
 - Fifth meeting in Trubia (Spain) organized by IQNSA (09/11/17)
 - Sixth meeting in Norwich (United Kingdom) organized by UEA (17/04/18)
2. Elaboration of a webpage to publicize the project: *supercoal.incar.csic.es*. It has been updated periodically.
3. Compilation and elaboration of the:
 - First Annual Report, covering the period from 1st July 2015 to 31st December 2015
 - Mid Term Report, covering the period from 1st July 2015 to 31st December 2016
 - Second Annual Report, covering the period from 1st July 2017 to 31st December 2017
4. Reporting to the Commission, in the framework of the following TGC2 meetings:
 - Forbach (France) on 17th May 2017
 - Cologne (Germany) on 19th April 2018
5. Discussion of the tasks to be performed and distribution of samples among partners
6. Elaboration and distribution of the minutes corresponding to the periodical meetings
7. Elaboration of the amendments for the change of the project's coordination. Rosa Menendez was replaced by Marcos Granda.

WP1. PREPARATION OF PITCH-LIKE PRODUCTS FROM COAL-DERIVED LIQUIDS AND COKES/GRAPHITES (IQNSA / UPB / CTRom)

Task 1.1 Polymerization of anthracene oil (IQNSA / UPB / CTRom)

Anthracene oil (AO) is a fraction obtained from coal tar (CT) by distillation, consisting on a mixture of polyaromatic (from 2 to 4 aromatic rings) hydrocarbons. The main components in this fraction are phenanthrene, anthracene, fluoranthene and pyrene. Thus, AO can be considered a residue from the Carbochemical Industry with a relatively low cost which can be used as raw product for the production high added value synthetic pitches.

IQNSA has been working in the last years in the synthesis of AO pitches to be used as different carbon precursors (carbon fibers, mesophase pitches, graphene precursors, etc.). It has been proved that these synthetic pitches could be good candidates to obtain graphene precursors, due to its absence of impurities (as quinoline insolubles, QI), high aromaticity and low content of heteroatoms. In addition, it has been also observed that it is possible to model the final crystal structure of graphene materials by controlling the chemistry of the polymerization process from which synthetic pitches are obtained.

In this context IQNSA has developed and produced at pilot scale anthracene oil pitches to be used as graphene (G) and activated carbon (AC) precursors.

The resulting product is a synthetic pitch obtained in the "Sedimentation & Product Output" stage. In some cases, it was necessary to adjust more finely the softening point of pitch. This operation was made in laboratory.

To obtain a synthetic pitch from AO it is necessary to promote a polymerization process between its molecules. Such polymerization process results in a mixture of oligomers enriched in naphthenic structures. In this way IQNSA has developed a process based on the use of the oxygen of the air. In this process AO is submitted to a thermal oxidative treatment in presence of oxygen, in which it is promoted the molecular growing trough polymerization reactions.

The resulting product is named "Reaction Product" and it is subsequently subjected to a thermal treatment (350-400 °C) under inert atmosphere (N₂). This thermal treatment is necessary to promote the creation of macromolecular flat structures. The aromaticity grows, and the oxygen coupled to the compound in the oxidative treatment is eliminated. This stage results in molecules with higher carbon content.

In a subsequent process the "Reaction Product" (RP A) can be modified to control its chemical structure resulting either in flat macromolecular or in three-dimensional structures where the molecular units are joined by cross-linking. The resulting structure will depend on the reaction conditions of the process. In this way short residence times and high temperatures result in planar aromatic structures and low temperatures and long residence time result in a crosslinked model. By this method ("oxidative way") it is possible to control the final crystal structure of the resultant graphite.

On the other hand, it is also possible to modify the final structure of the coke and the graphite by the addition of a phenolic additive ("Chemical way") which promotes the crosslinking (RP B). It is important to remark that this additive is a product obtained as a residue in the industrial process of IQNSA, also contributing to the economic viability of the project.

Eventually the resulting products are distilled to obtain the synthetic pitch. In this distillation stage the softening point (SP) of the resulting pitch is adjusted depending on the final use. In this project the distillation process has been taken as far as possible to eliminate as much volatiles as possible. This results in better yields of the eventual coking process.

This is a very versatile process which allows controlling some reaction conditions (residence time, stirring, pressure, temperature, etc.) to obtain different carbon materials to be used as activated carbons and graphene precursors.

About 100 L of both oxidative and chemical way products (RP A and RP B, respectively) were obtained.

Different samples of reaction products from the oxidative polymerization of AO were obtained: RP-AO-QN-01, RP-AO-QN-02, RP-AO-QN-03, RP-AO-QN-04, RP-AO-QN-05 and RP-AO-QN-06. The different reaction conditions investigated are shown in Table 1.1.

Table 1.1 Reaction conditions for the oxidative polymerization of AO

<i>Reaction product</i>	<i>Temperature (°C)</i>	<i>Pressure (bar)</i>	<i>Air flow rate (mL min⁻¹)</i>	<i>TG Conversion (%)</i>
RP-AO-QN-01	375	18	161	29.0
RP-AO-QN-03	350	18	161	22.6
RP-AO-QN-04	350	18	250	28.3
RP-AO-QN-07	325	18	161	21.2
RP-AO-QN-08	300	18	317	32.2

Moreover, some reaction conditions were tested in the "Oxidative way" for sample RP-AO-QN-04. During this studio it was observed the great importance of air flow rate for controlling the polymerization grade of the reaction product (Table 1.2).

Table 1.2 Reaction conditions tested.

<i>Reaction product</i>	<i>Temperature (°C)</i>	<i>Reaction Product Inlet (L h⁻¹)</i>	<i>Air flow (g h⁻¹)</i>	<i>Residence time (h)</i>	<i>Conversion (%)</i>
RP-AO-QN-04A	250	5.0	875	2.75	41
RP-AO-QN-04B	250	4.0	700	2.85	40
RP-AO-QN-04C	250	4.0	600	2.85	36
RP-AO-QN-04D	250	4.0	450	2.85	36
RP-AO-QN-04E	250	4.0	400	2.85	33

In addition, the process conditions to produce the two types of AO pitches, which have turned out to be the optimal precursors of graphite for the production of graphene, were optimized. The samples were,

- Type A: Precursor of highly oriented coke structure with a needle and flow domains optical texture
- Type B: Precursor of coke with a fine mosaics optical texture

For the production of these types of pitches, different operating conditions were required.

For type A the most convenient temperature was around 350 °C. At this temperature the reactivity of AO with air was high and it was needed to minimize the residence time so that conversion did not exceed 30 %.

At higher conversion rates the formed pitch reacted again increasing the molecular weight of pitch components, which was not desired as it makes more difficult obtaining a highly fluid system capable of forming highly oriented crystalline textures during the subsequent carbonization. Figure 1.1 shows the evolution time of reaction yield versus percentage of the product out of exclusion limits, determined by SEC.

Treatments at 375-380 °C for 3-4 h of soaking time were revealed as promising treatments for improving pitch properties, specially wettability and rheology.

On the other hand, type B pitches required more moderate temperatures (around 250 °C), reaching higher conversion rates (50 %). The preparation of this type of pitches required high stirring conditions with a high share impeller during the distillation step.

For the preparation of both type of pitches, pressure was adjusted according with the different reaction temperatures. High pressures were required to decrease the volume of the bubbling air. It was recommended to operate around 10 bars above the equilibrium vapour pressure. Feeding air flow should have been also adjusted to avoid oxygen in the exhaust gases. The presence of oxygen can be dangerous once the gases leave the reactor. Nevertheless, the presence of oxygen in the vapour phase promotes gas phase cracking reactions with soot-like particles production. This is especially recommended to produce type A pitches where the process requires higher temperature.

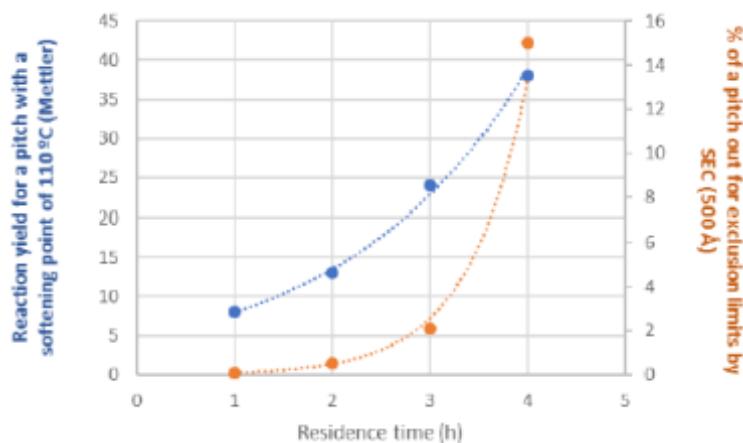


Figure 1.1 Evolution in time of Anthracene Oil reacting at 350 °C, 20 bar and 300 g/h of feeding air

The same anthracene oil used to obtain these “Reaction Products” was submitted to the Romanian partners UPB/CTRom. One of their specific objectives for this project has been the development of the equipment required by the project needs for “an unconventional oxidative thermal treatment of AO assisted by microwave heating in a discontinuous small-scale reactor”.

Given the high degree of novelty of the microwave technology applied to polymerization of the anthracene oil, UPB and CTRom developed a small-scale experimental laboratory module equipment no. 1 - single mode applicator, to study the process in a preliminary phase, Figure 1.2. The main constructive requests for the technological assembling were described and the process design included: design principle scheme, working conditions, constructive and functional specificity of the equipment. Programming and control system were finalized after completion of the small-scale equipment itself to be optimally adapted to specific operating conditions. The execution documentation was elaborated by UPB and provided to CTRom. UPB gave technical assistance during the entire period of equipment execution, starting-up/commissioning until reaching the operation parameters.



Figure 1.2 Small scale laboratory equipment for the experimental model - Single mode applicator

Main parameters used:

- (i) Capacity: up to 10 mL of AO.
- (ii) Reaction conditions: AO polymerization temperatures between 250-380 °C with residence times of 1-5 hours. The oxygen (air) flow (rate of 20-30 wt. % air/AO) and microwave power were carefully controlled.
- (iii) Microwave reactor: contains a single/monomode applicator with a small capacity quartz reactor having an oxygen/air inlet pipe, also with the role of stirring. Reaction parameters used: heating rate up to 5 °C min⁻¹; temperature above 350 °C; soak time between 3-5 hours.

14 experiments in microwave field (amount varying between 7-32 g) and 9 experiments in conventional heating were performed. The temperature profiles of the microwave experiments are shown in Figure 1.3 (*First Annual Report and Mid Term Report*).

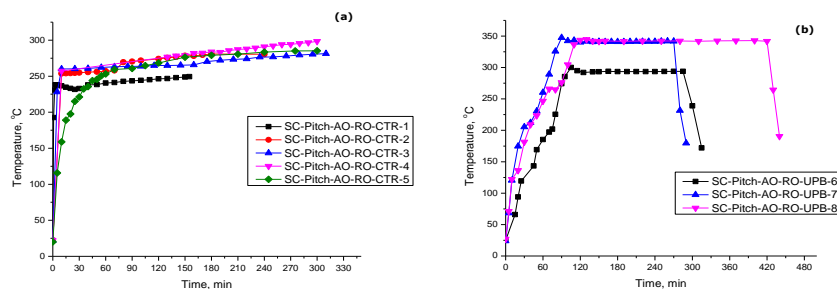


Figure 1.3 Temperatures profiles (a - microwave heating; b - conventional heating)

After running the lab scale tests (phase I single mode applicator) within the unconventional discontinuous small-scale reactor, CTRom, based on its own engineering, started the construction of a preliminary equipment having 1 (one) microwave generator and after that, 3 (three) microwave generators (phase II-multimode, Figure 1.4). The semi-pilot equipment (equipment no. 2 multimode applicator) was used to obtain the preliminary information necessary for scaling-up the process. Conclusions drawn from experiments in phase I were confirmed by the phase II of oxidative microwave heating of AO. It was found that temperature above 350 °C, a slow gradient (2-5 °C min⁻¹) and oxidation time up to 5 hours are suitable parameters to obtain pitches with interesting softening points (*Mid Term Report*).

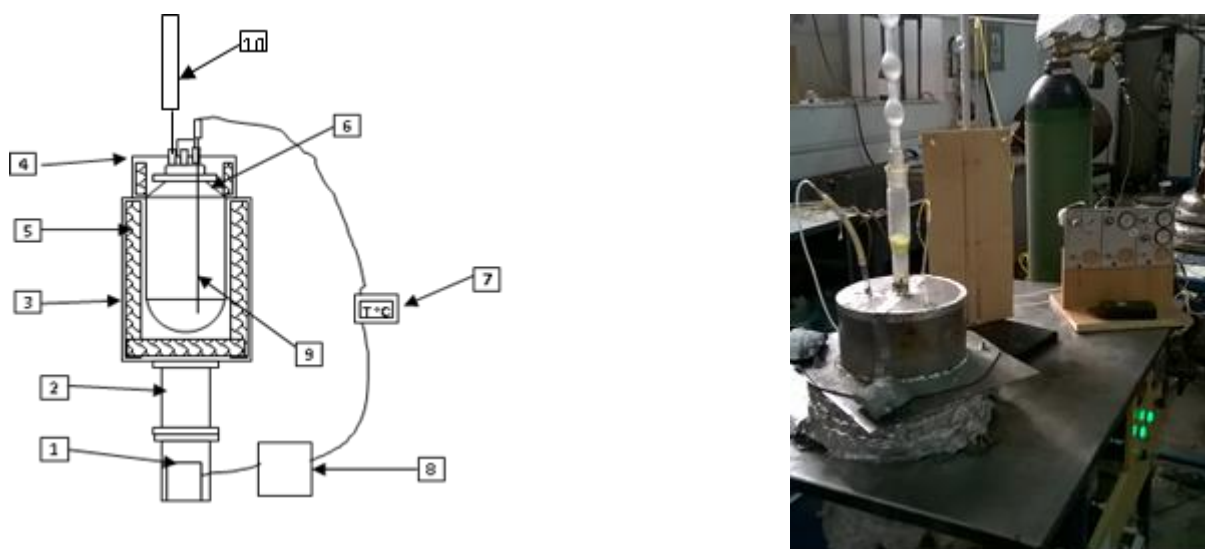


Figure 1.4. (Left) Schematic diagram of the multi-mode experimental microwave reactor (1. Microwave generator; 2. Waveguide; 3. Applicator; 4. Lid; 5. Thermal insulation; 6. Quartz reactor; 7. Temperature controller; 8. Power control; 9. Thermocouple, 10. Condenser system). (Right) Semi-pilot equipment (II)

Pitches were obtained following 2 process schemes:

- Scheme 1: AO was thermally treated in the presence of air flow with low/high heating rates, followed by distillation (CTRom).
- Scheme 2: AO was thermally treated at 290 °C (conventional heating) and the resultant distillation residue was taken as pitch-like precursor for the microwave heating experiments. Distillation up to 290 °C of AO was performed to remove components with relatively low boiling points, which do not contribute substantially to polymerization reactions/condensation, occurring during oxidative heat treatment in oven. By thermal stabilization of AO through distillation up to 290 °C and removing a percent of about 7 % components with relatively low boiling points, do not contribute substantially to polymerization reactions/condensation.

During 2017 both partners CTRom and UPB carried out the targeted experiments to obtain from an initial amount of AO varying between 200-1400 g suitable amounts of AO pitch (around 150 g) of representative pitches. The experiments were also carried out by using conventional heating for comparative purposes.

13 experiments of which 10 samples of AO pitch were supplied to INCAR-CSIC for further trials: SC-PT-AO-CTR-18, SC-PT-AO-CTR-19, SC-PT-AO-CTR-20, SC-PT-AO-CTR-21, SC-PT-AO-CTR-22-1,

SC-PT-AO-CTR-23, SC-PT-AO-CTR-24, SC-PT-AO-CTR-26, SC-PT-AO-CTR-27 and SC-PT-AO-CTR-28).

Electric energy consumption studies during conventional and microwave heating were evaluated and enclosed in *Appendix 2, Second Annual Report*. It was preliminary proven that the average value of 165 Wh of electric energy consumption in case of experiments carried out by microwave heating showed a considerable decrease of 62.6 % compared to the electric energy consumption of 441 Wh for conventional heating.

These results are a proof of concept according to which the heating in microwave field provide benefits on the time of heat treatment and energy consumption, although at experimental laboratory semi-pilot stage. The experiments confirmed also the basic principles of microwave heating according to which energy is conducted directly to materials through molecular interactions and electromagnetic waves are transformed into heat inside the particles. Moreover it has been demonstrated that: i) up to the reaction temperature ($< 290\text{ }^{\circ}\text{C}$) the total energy consumed during the preliminary phase of AO heating by microwave, requires a lower energy intake of only 27.7 % (needed to heat the core of the sample) comparing to 73.8 % in case of conventional heating (according to which energy is transferred to material through convection, conduction and radiation of heat from the surface of the material); ii) during the polymerization stage of AO ($> 290\text{ }^{\circ}\text{C}$) the total energy consumed requires 72.3 % of the total energy comparing to 26.2 % in case of the conventional heating.

Experiments were carried out by permanent consulting between UPB and CTRom teams. Thus, oxidative heat treatment in microwave field realized by CTRom was followed step-by-step by characterization of AO pitch-like products by UPB team.

Conclusions drawn from experiments in semi-pilot phase were confirmed by the oxidative microwave heating of AO. It was found that a temperature between $340\text{--}350\text{ }^{\circ}\text{C}$, a slow gradient ($2\text{--}5\text{ }^{\circ}\text{C min}^{-1}$) and oxidation times by 3-5 hours, favours the production of characteristic pitches with interesting softening points (*Second Annual Report*).

According to the Task 1.1 CTRom scaled-up the process and designed and manufactured a pilot scale equipment (equipment no. 3, Figure 1.5) for polymerization of AO using an innovative technique based on direct microwave heating. During 2017-2018 both partners CTRom and UPB carried out the targeted experiments to obtain the AO pitch polymerization in pilot microwave demonstrator equipments of larger capacity (5000 mL), enclosed in *D.3.2, present Final Report*.

Main parameters used:

- (i) Total Capacity: 5000 mL of AO; reactor capacity: 1000 g of AO pitch
- (ii) Reaction conditions: AO polymerization temperatures of max. $400\text{ }^{\circ}\text{C}$ and atmospheric distillation, with residence time of 2-3 hours. The oxygen (air) flow (rate of 20-30 wt. % air/AO);
- (iii) Microwave reactor: 2.45 GHz frequency and 3 kW minimum power energy.

Being equipped with a special designed gas admission system coupled with a paddle stirrer containing aligned nozzles, operation of different process stages can be easily controlled (distillation, oxidation).



Figure 1.5 Microwave pilot scale equipment for polymerization of anthracene oil (general view)

Two (2) representative pitches (sample 1: SC-PT-AO-CTR-31 and sample 2: SC-PT-AO-CTR-32) were produced in large amount (by 1500 g starting from an initial amount of 4000 g each) that have been supplied to INCAR-CSIC for further characterization and trials.

These experimental pilot stage results are a proof of concept according to which the heating in microwave field provide benefits on the time of heat treatment and energy consumption. The experiments reconfirmed the basic principles of microwave heating according to which energy is conducted directly to materials through molecular interactions and electromagnetic waves are transformed into heat inside the particles.

Experiments were carried out by permanent consulting between CTRom and UPB teams. The oxidative heat treatment in microwave field realized by CTRom was followed step-by-step by characterization of AO pitch-like products by UPB team.

The procedure of microwave synthesis of pitch was carried-out in two steps:

- Thermal treatment (distillation step) of the corresponding AO in a microwave reactor under N₂ flow up to 295 °C (to remove low weight hydrocarbons).
- Thermal treatment of the corresponding AO distillation residue in a microwave reactor under N₂ flow from 295 to 335 °C (0.2 C min⁻¹).
- Oxidation treatment of the previous precursors in a pilot reactor (under N₂ flow) at 335° C with 18.7 % air.
- Distillation treatment of the pitch-like products for 5 hours: at 370 °C (sample 1: SC-PT-AO-CTR-31) and at 360 °C (sample 2: SC-PT-AO-CTR-32). The preparation of this type of pitches required high stirring conditions during the distillation step.

Conclusions drawn from experiments in pilot and final phase are confirmed by the oxidative microwave heating of AO. It was found that a temperature up to 335 °C, a slow gradient (2-5 °C min⁻¹) and oxidation times by 2-3 hours, favours the production of characteristic hard pitches with Mettler softening points over 90 °C.

Based on all this data and experimental observations, a few conclusions can be drawn:

- AO has tendency to increase the distillation rate with increase the microwave power;
- After reaching boiling point (270-272 °C) the heating process to the target working temperature is improved if there are a few distillation steps;
- An important thing is improving the sealing of chemical reactor and all the connections with different devices.
- Decreasing heating thermal gradient improve the oxidation process and has influence on the final conversion.

Task 1.2 Preparation of QI-free coal tars (IQNSA)

IQNSA has developed a quinoline insoluble (QI) removal process from coal tar consisting on sedimentation of the QI particles under controlled temperature and pressure. The process was carried out under stirring in a special reactor, where the coal tar was firstly heated to achieve good rheological conditions. Additionally, an aliphatic additive was introduced to modify the surface tension of the medium, making the QI particles to flocculate to eventually settle down. The combination of those conditions (pressure, temperature, stirring and flocculation) allowed the sedimentation of the QI particles arising two different phases in the reaction tank: a top fraction (overflow) with a low QI content and a bottom one (underflow) where the QI content of the whole sample settled down.

The process can be divided in three different steps:

1. Firstly, the mixture is heated (150-250 °C) under pressure conditions (5 bars) to get the necessary rheological conditions of the medium for the QI sedimentation. Over pressure it is necessary to keep the mixture over the vapor pressure at these temperature conditions, to prevent the mixture from boiling which avoid the QI particles settle down.
2. Then a stirring step (500 rpm, 1 h approximately) is necessary to homogenize the product. The main goal of this stage is to allow an intimate contact between the aliphatic additive and the QI particles present in the mixture.
3. Finally, before the homogenization process, the stirring is stopped, and the product is held at this temperature for 1.5 h under over-pressure conditions (5 bars) allowing the QI settle down.

Both overflow and underflow phases can be taken out from the sedimentation tank in a continuous way, while new coal tar feeds the tank. In this way it is possible to work in a continuous mode to achieve enough quantities of QI-free coal tars.

The QI-free tars obtained from this method must be distilled to obtain the corresponding pitches. To increase the final yield in the coking process is necessary to remove as much QI as possible getting a high softening point of the pitch.

An impregnation pitch (SC-PT-LIQ-QN-01) was obtained by this QI removal process. To improve the final yield a low softening point pitch was used as raw material (SP ~ 60 °C). In this case the mixture had to be heated at a slighter higher temperature than used with coal tar (250 °C).

The final yield obtained in the QI-free pitch was 51 %. This batch was distilled to increase its softening point (up to 88.5 °C).

IQNSA was also working to obtain a sample from a tar for which it was not necessary to eliminate the content in QI particles given its very low concentration.

In this sense IQNSA supplied to the Romanian partners 15 kg of pitch with a 90 °C Mettler softening point.

The pitch was distilled directly in the lab from a standard coal tar with a very low QI content (< 0.5 %). IQNSA selected the tar due to the QI content and its rheological behavior that produce large flow domains optical texture in its derived cokes.

Although IQNSA produces this pitch industrially, it has been chosen to provide the laboratory scale sample so that it can be compared with the anthracene oil pitch. Distillation would be an issue for scaling up the process.

Task 1.3 Characterization of raw materials and pitch-like products (IQNSA / UPB)

IQNSA has carried out a preliminary characterization to analyze the suitability of the conventional raw materials (Tables 1.3 to 1.5) and coke precursors obtained (the pitches resulting from the distillation of the above-mentioned Reaction Products synthesized by conventional heating. This company has the proper equipment to carry out the analysis needed to give data about the potential crystalline structure of resultant cokes and their aromaticity.

Table 1.3 Analysis of A.O used as raw material

Parent A.O Analysis	
Density g cm⁻³	1.098
Water (wt. %)	0.1
Sulfur (wt. %)	0.0
QI (wt. %)	0.0
TI (wt. %)	0.0
Distillation curve	
1% (°C)	285
5% (°C)	293
10% (°C)	297
20% (°C)	318
50% (°C)	347

Table 1.4 Characteristics of the AO pitches

<i>Sample</i>	<i>TI (wt. %)</i>	<i>AI (wt. %)</i>	<i>SP (°C)</i>	<i>CF (wt. %, SERS)</i>
SC-PT-AO-QN-08	23.4	1.0	99.1	43.7
SC-PT -AO-QN-07	25.1	0.4	110	46.3
SC-PT-AO-QN-04	59.3	1.0	>200	60.0
SC-PT-AO-03 A	71.2	111.1	>200	82.8
SC-PT-AO-03 B	70.0	101.2	>200	87.3
SC-PT -AO-QN-01	28.0	0.3	110.5	44.3

Table 1.5 Characteristics of the coal tar pitches before and after the QI removal

<i>SAMPLE</i>	<i>SP (°C)</i>	<i>CF (wt. %, SERS)</i>	<i>TI (wt. %)</i>	<i>AI (wt. %)</i>
SC-PT-LIQ-QN-01 (after distillation)	88.5	39.6	14.7	1.9
SC-PT-LIQ-QN-01_0 (after sedimentation)	N/A	N/A	N/A	0.2
SC-PT-HIQ-QN-01	60.0	32.2	11.5	6.0

UPB and CTRom have also carried out a preliminary characterization of the AO and the pitch provided by IQNSA following standard physical-chemical procedures applied to coal derived products (*First Report, Mid Term and Second Annual Report*). Briefly, carbon enrichment in the reaction products is variable with increasing the temperature by 380 °C and by increasing the duration of the air blowing from 0.5 to 2.5 h, confirming the need for a longer reaction time.

For the samples that have been analysed the results have shown that samples SC-PT-AO-CTR-18, 19, 20, 23 and 24 are mainly composed of carbon (> 88.8 wt. %) and, to a lesser extent, hydrogen and oxygen. Nitrogen in all cases only account for less than 1.5 wt. %. Oxygen contents in the reaction products were slightly higher than in the parent AO. These findings are consistent with the introduction of oxygen occurring mainly during the oxidative treatment and part of this oxygen being lost during subsequent thermal treatment to produce pitch.

Solubility parameters (TI and QI) showed higher percentages (between 30-65 wt. % for TI and around 20 wt. % for the QI) in case of longer heating and oxidation time of over 4-5 h.

Softening Point varied between 50-221 °C. There are only a few samples for which the softening point is higher than 90 °C.

The results proved the high purity of AO sample provided by IQNSA. The absence of QI and, thus, high purity carbon precursor assures structure continuity and favours the formation of anisotropic carbon, properties that will be able to produce active materials with determined characteristics of morphology, microstructure, surface chemistry and electrical conductivity targeted in our project. 19 samples of pitch-like products were characterized in 2017 (proximate analysis, softening point, solubility parameters TI, QI) following the Romanian and ASTM standards used in UPB laboratory (*Appendix 2, Second Annual Report*).

The results fall in the limit values for such type of products. Remarkable are the samples: SC-PT-AO-CTR-19, SC-Pt-AO-CTR-20 and SC-PT-AO-CTR-21, with softening points of 89, 97 and 221 C, respectively. These samples showed also an increased carbon content ranging between 88 - 91.5 wt.%. The information obtained in this task was used to assess the effect of the composition and properties of the coal-derived liquids on their conversion to isotropic/mesophase pitches and coke/graphite precursors with the desired characteristics.

During the pilot experiments carried out in the final stage of the project 2017-2018 two representative pitches (sample 1: SC-PT-AO-CTR-31 and sample 2: SC-PT-AO-CTR-32) were produced in large amounts (by 1500 g each) that have been supplied to INCAR-CSIC for further characterization and trials Table 1.6. The details are presented in *Deliverable D3.2* of the present *Final Report*.

Table 1.6 Main characteristics of the AO pitch samples

No.	Sample ID	Yield wt. %	VM ^{db} wt. %	FC wt. %	SP (°C Mettler)	TI wt. %	QI wt. %
1	SC-PT-AO-CTR-31	40.8	68.46	31.54	91.1	17.78	<0.2
2	SC-PT-AO-CTR-32	32.5	61.17	38.83	111.7	24.44	<0.2

MV= volatile matter; db=dry basis; FC=fixed carbon; SP=softening point (Mettler, ASTM); TI=toluene insoluble; QI=quinoline insoluble

For both samples the most convenient temperature of oxidative treatment was around 335 °C. At this temperature the reactivity of AO with air was high and it was needed to decrease the residence time during conversion.

Sample 1 required treatments at 370 °C for 5 h soaking time revealing higher conversion rates (by 41 %) for improving pitch properties.

Sample 2 required a moderate temperature (at 360 °C for 5 h soaking time), reaching lower conversion rates (32.5 %).

Briefly, carbon enrichment in the reaction products is variable with increasing the temperature by 335 °C and by increasing the duration of the air blowing from 2 to 3 h, confirming the need for a longer reaction time. The fixed carbon results fall in the limit values for such type of products. These samples showed also a carbon content by 40 wt. %, considered as adequate for a pitch-like product.

Softening Point (Mettler, ASTM standards) varied between 91.1-111.7 °C.

Solubility parameters (TI and QI) show percentages between 17-25 wt.% for TI and under 0.2 wt.% for QI in case of longer heating and oxidation time of 5 h.

The results proved the high purity of AO sample provided by IQNSA. The absence of QI (under 0.2 wt. %) and, thus, high purity carbon precursor assures structure continuity and favours the formation of anisotropic carbon, properties that will be able to produce active materials with determined characteristics of morphology, microstructure and surface chemistry targeted in our project.

The information obtained in this task was used to assess the effect of the composition and properties of the coal-derived liquids on their conversion to isotropic/mesophase pitches and coke/graphite precursors with the desired characteristics.

Task 1.4 Preparation and characterization of cokes and graphites (IQNSA / UPB / CTRom)

IQNSA has a specific coking furnace (its design, optimization and process description are described in Task 2.2) to synthesize coke samples from the different carbon precursors obtained in the Pilot Plant.

Additionally, some cokes obtained from the second step (also from the oxidative polymerized AO) were also supplied to INCAR-CSIC to be used as precursors of graphite: SC-CK-AO-QN-01, SC-CK-AO-QN-03A, SC-CK-AO-QN-03B, SC-CK-AO-QN-4, SC-CK-AO-QN-07 and SC-CK-AO-QN-08.

The obtained cokes have been characterized by optical microscopy. This technique can be used to study anisotropic structures due to its capacity to reflect polarized light in different directions depending on the orientation of the crystallographic domains. Moreover, this technique can determine the crosslinking grade effect, homogeneity of medium, regularity of crystal structure, etc. The obtained micrographs are shown in Figure 1.6.

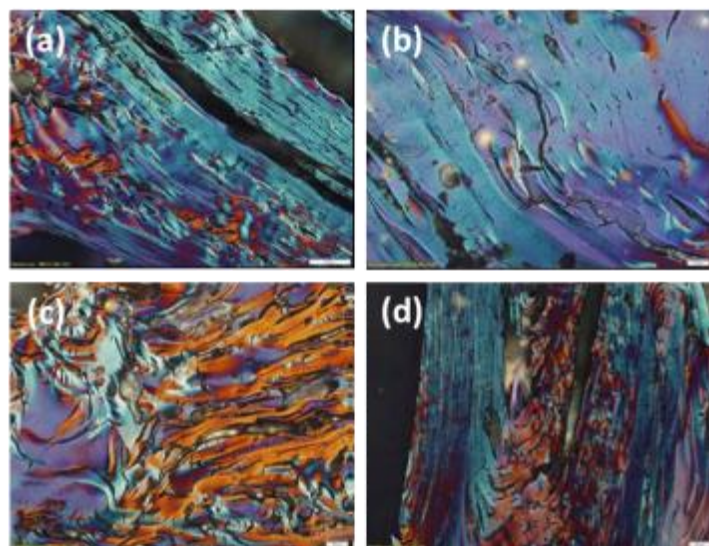


Figure 1.6 Optical micrographs of (a) SC-CK-AO-QN-01 (b) SC-CK-AO-QN-03 (c) SC-CK-AO-QN-07 and (d) SC-CK-AO-QN-08

As it can be seen in cokes SC-CK-AO-QN-01, SC-CK-AO-QN-03, SC-CK-AO-QN-07 and SC-CK-AO-QN-08 there is a completely lack of QI agglomerates or any other impurity as they come from anthracene oil, a fraction of coal tar pitch distillation. In addition, it can be observed a needle arrangement in crystal domains, especially in samples SC-CK-AO-QN-01 and SC-CK-AO-QN-08, with a fluid domains crystal structure. Those characteristics could allow the generation of a good crystal structure for the synthesis of graphene. It was observed a slight difference between the crystal structure of cokes SC-CK-AO-QN-01/08 and SC-CK-AO-QN-03/07. This difference can be attributed to the different distillation conditions in pitch generation, especially the distillation rate. Controlling these reaction conditions, it could be possible to obtain an intermediate crystal structure or a more needle one.

IQNSA has produced (and supplied, as precursor for the synthesis of graphene materials) a high crystallinity coke (SC-CK-CT-QN-01) from the QI-free coal tar produced in Task 1.2. This coke was preliminary characterized by optical microscopy (Figure 1.7).

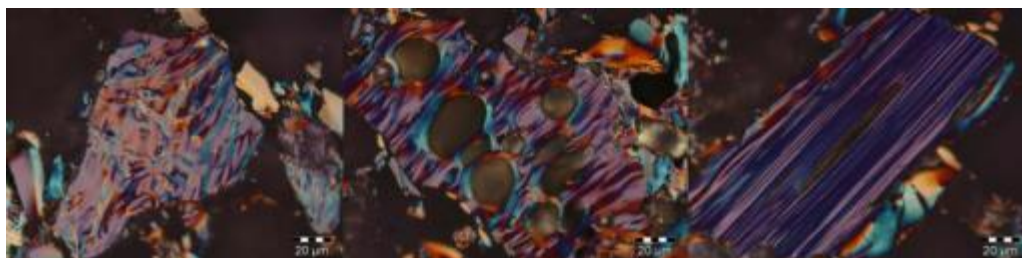


Figure 1.7 Optical micrographs of SC-CK-CT-QN-01

UPB and CTRom have prepared low temperature cokes from pitch-like products obtained by AO oxidative polymerization in microwave field. This represented a novel approach to test the ability of a carbon material precursor as “absorbing material” to enhance the rate of pitch pyrolysis in the microwave field. Two experimental equipments were used to obtain the pitch cokes: a conventional heating one and a semi-pilot preliminary equipment heated by microwaves, both created by CTRom. Different experimental parameters were tested to afford the best conditions. Because temperature measurement is a challenging aspect under microwaves, experiments were carried out using an infrared temperature sensor. A comparison of the data obtained from temperature-time together with the yields and analysis of products of conventional heating (UPB) and microwave pyrolysis (CTRom) were considered (*First Annual Report, Mid Term Report Second Annual Report*). Two different heating equipments were used:

Conventional equipment, equipment no. 4, Figure 1.8 (left): created within the 1st phase of project by CTRom, based on the technology proposed by UPB, to carry out the AO pitch coking experiments. Different experimental parameters were tested to afford the best heating conditions.

Parameters tested: temperature and heating rate were investigated with a special attention to how they affect the yield. Coke was obtained during a wide range of temperatures varying from low to high: 480-500 °C (green coke), 600-700 °C and 1000-1300 °C, all under nitrogen flow.

Unconventional (microwave) equipment, equipment no. 5, Figure 1.8 (right): realized by CTRom with 3 MW generators, each having absorption of 4.5 KW power of a total of 13.5 KW capable of delivering up to 9 KW of microwave power inside the oven, which represents a new approach to enhance the rate of pitch-like pyrolysis in the microwave field.

Parameters tested: temperature, MW power and precursor mass with a special attention to how they affect the yield. Cokes characterization was carried out by standard procedures (proximate analysis, real density, apparent density, porosity; iodine value was checked before coke activation) as well as by optical microscopy.



Figure 1.8 (Left) Pilot conventional heating device, equipment no.4. (Right) Cylindrical applicator with wave guides of preliminary microwave equipment no.5

For obtaining semi - coke, different temperatures were selected (600, 650 and 700 °C) in order to compare the final results with those obtained by conventional heating for the same temperatures. Beside these, were selected another temperatures (500, 680, 1000 °C) in order to observe modifications. The soak time for the comparative tests was selected to be 0.5 hour instead of 1 hour for the conventional tests. The heating time in the microwave was four times lesser than conventional heating knowing that the thermal gradient for conventional was 2 °C min⁻¹. For the comparative tests a cylindrical alumina crucible with 500 cm³ of capacity was used. The pitch sample weight was the same for all three temperatures (150 g).

Special emphasis was given to the differences found in the final products by conventional and unconventional treatments characterizing the cokes by standard procedures (proximate analysis, real density, apparent density, porosity) as well as by optical microscopy.

20 samples of low temperature pitch cokes were characterized in 2016-2017 (proximate analysis, real density, apparent density, porosity) following the Romanian standards used in UPB laboratory (Mid Term Report). Real density accounts values comparable for conventional-microwave heating and AO pitch and pitch IQNSA ranged between 1.5-1.87 g cm⁻³. Opened porosity is twice higher in case of microwave heating (50-72 wt. %) than conventional heating. This can be explained by the increased heating rate used during some microwave trials which determine the fast melting and swelling of the pitch mass and expansion of the volatile within the early coking stages. Fixed carbon increases with temperature and in all cases ranges between the same values for conventional (94.8-99.2 %) and unconventional heating (91.4-99.5 wt. %) Iodine value shows different levels that should be further investigated. One example is for sample SC-CK-AO-CTR-03 pyrolyzed in microwave field at 700 °C (180.29 mg g⁻¹). Both experimental pitches (AO pitch supplied by CTRom and pitch supplied by IQNSA) pyrolyzed in conventional and unconventional (microwave) conditions exhibited similar optical textures, suggesting that the structural order in the cokes could be mainly defined by the characteristics of thermal cycle (Figure 1.9).

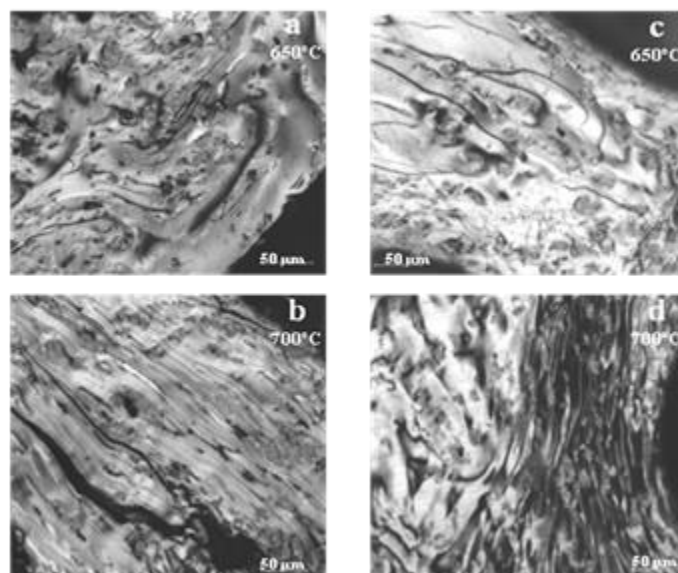


Figure 1.9 Optical micrographs of (a, b) SC-IP-CK-UPB-04 and SC-IP-CK-UPB-05 in conventional heating and (c, d) SC-IP-CK-CTR-02 and SC-IP-CK-CTR-04

The formation and development of optical textures of coalesced mesophase (domains) of large regions were identified in low temperature cokes obtained from both samples; also, optical textures of mosaics on small to coarse surface was produced; the decrease in the size of the domains observed for samples processed at lower temperatures (600 °C) under less severe conditions appear to be related to changes in the molecular structures of the pitch samples. At higher temperature (650 - 700 °C) larger domains were observed, and this originates samples containing larger mesophase spheres in a less viscous environment. Coke samples showed (on both conventional and microwave heating) an increase of the anisotropic intensity which proves more complex and optically oriented structures.

According with the objectives of the task, new cokes were produced (in terms of conventional and non-conventional heating) by using new laboratory equipment specially designed. In the D1.1 and D1.2 delivered (*Mid Term Report*), the concept and the pre - designed microwave heating equipment for coking of AO pitch were presented. It was designed a device in order to obtain high temperatures for the synthesis of semi-coke and coke from pitch. Moreover, it was also presented the justification for choosing the multi-mode cylindrical applicator, in which the samples can be placed in the maximum field of the microwave with the help of a dedicated pattern of windows layout for microwave injection. After performing the proposed experiments, CTRom assisted by UPB build a new multi-mode model based on acquired knowledge (*Second Annual Report*).

14 AO pitch samples (obtained in a reasonable amount for further trials) were used as raw material for coking tests. 7 (seven) of these samples were pyrolyzed in conventional heating and the other 7 (seven) samples were pyrolyzed in microwave heating. Also, 6 (six) IP-pitch samples were used as raw materials for coking tests. The pitch cokes were characterized in terms of proximate analysis, real density, apparent density, porosity and microscopy, following the standards used in UPB laboratory, (*Second Annual Report*).

Both experimental pitches (AO pitch supplied by CTRom and isotropic pitch supplied by IQNSA) pyrolyzed in conventional and unconventional (microwave) conditions exhibited similar optical texture, suggesting that the structural order in the cokes could be mainly defined by the characteristics of thermal cycle.

Coke samples pyrolyzed at 480-500 °C show highly developed optical texture. This seems to indicate that mesophase spherules had enough time to nucleate and grow, and to associate as chains of mesophase spherules. Increase by up to three times the heating rate in case of using microwave (9-10 °C min⁻¹) allowed mesophase enough time to nucleate and coalesce and grow in highly developed optical textures.

The optical texture developed from mesophase coalescing show very similar aspects for both heating technologies in creating almost the same precursor optical type of the pitch green coke. Cokes obtained under these experimental conditions show a preferential optical texture of domains, these domains being larger in size as increase the temperature of coke preparation.

Tests have revealed similarities in the characteristics of pitch cokes obtained in microwave field compared to those obtained by conventional heating (see *Second Annual Report*) for comparative

purposes). Remarkable is that these features, highlighted by the physical and chemical parameters, are supported by the microscopic studies. The same parameters and optical texture appearance were obtained at the same temperature but with heating rate of about 4 times faster (or more) and the soak time at of up to 85% lower when using microwaves. This is a further proof of the fact that the type of heating generated through microwaves straight in the centre of the sample - determines the same chemical transformation as compared to conventional heating by convection slower and of much longer duration and the same morphological and structural changes identified by microscope. Smaller soak times and faster heating rates are the main parameters recommending microwaves as a technology that involves lower consumption of energy compared to the classic one.

In the last stage of the project 2017-2018 UPB assisted CTRom to obtain green cokes by microwave heating (in order to produce the corresponding activated carbon) using the pilot equipments created especially for this project. An adequate amount of samples was provided within the pilot device, equipment no.6, Figure 1.10.



Figure 1.10 Pilot scale equipment assisted by microwave for preparation of carbon precursors and activated carbon, equipment no.6.

CTRom/UPB produced in the last stage of the project 6 (six) coke samples which were supplied, as precursor for the synthesis of graphene materials to INCAR, as follows: 2 (two) increased crystallinity cokes obtained from sample 1 (samples SC-CK-AO-CTR-10 and SC-CK-AO-CTR-11) and 4 (four) cokes obtained from sample 2 (samples SC-CK-AO-CTR-12, SC-CK-AO-CTR-13, SC-CK-AO-CTR-14 and SC-CK-AO-CTR-15), in Task 1.1.

The pilot equipments used to obtain the pitch cokes by microwaves was performed by CTRom. Different experimental parameters were tested to afford the best conditions. Because temperature measurement is a challenging aspect under microwaves, experiments were carried out using an infrared temperature sensor. A comparison of the data obtained from temperature-time together with the yields and analysis of products (UPB) of microwave pyrolysis (CTRom) were considered. According with the objectives of the task, green cokes of 450 and 480 °C under nitrogen flow, were produced (in terms of microwave heating by using new laboratory equipment specially designed for this purpose).

Main parameters used:

Equipment: The coking microwave equipment realized by CTRom comprises 3 MW generators, each having absorption of 4.5 KW power of a total of 13.5 KW capable of delivering up to 9 KW of microwave power inside the oven, which represents a new approach to enhance the rate of pitch-like pyrolysis in the microwave field. The synthesis was performed in nitrogen, flow rate of 1.2 L min⁻¹.

Parameters tested: temperature, MW power and precursor mass with a special attention to how they affect the yield. Cokes characterization was carried out by standard procedures (proximate analysis, real density, apparent density, porosity; iodine value was checked before coke activation) as well as by optical microscopy.

Mechanisms: During pitch low temperature carbonization the step before chemical activation process the chemical reactions generate char, vapours and tars. Besides decomposition reactions, other chemical reactions take place as: condensation, polymerization, reduction etc.

At 450-480 °C the edges of C-C cross-linked structures start to lose their stability because of polymerization. One part remains unsaturated and others react with H₂, becoming saturated. The first are volatilized as vapours and the last are condensing as char with a high content of aromatic hydrocarbons.

During the final reporting period, two (2) AO pitch samples were used as raw material for coking tests. 6 (six) sub-samples each of 300 g were pyrolyzed in microwave heating. The pitch cokes were characterized in terms of proximate analysis, real density, apparent density, porosity and optical microscopy, following the standards used in UPB laboratory.

Both experimental pitches pyrolyzed in microwave field at 450 and 480 °C exhibited similar optical texture, suggesting that the structural order in the cokes could be mainly defined by the characteristics of thermal cycle.

The data regarding its advanced characterization was summarized in Table 1.7.

Table 1.7 Preparation of AO green cokes in microwave field - parameters and characteristics

Coke sample ID	Parent pitch ID	Microwave coking characteristics							Coke characteristics				
		Y wt. %	T °C	Hr °C min ⁻¹	S min	M %	A ^{db} %	VM ^{db} %	FC wt.%	AD gcm ⁻³	RD gcm ⁻³	P %	IV mgg ⁻¹
SC-CK-AO-CTR-10	SC-PT-AO-CTR-31	42	450	14.5	60	0.04	0.21	25.16	74.63	-	-	-	173.23
SC-CK-AO-CTR-11		43.4	480	7.6	120	0.76	0.28	5.24	94.48	0.744	1.4714	49.44	288.18
SC-CK-AO-CTR-12		79.9	450	7.2	120	trac e	0.19	35.15	64.66	-	-	-	145.13
SC-CK-AO-CTR-13	SC-PT-AO-CTR-32	83.4	450	7.8	180	trace	0.03	43.90	56.07	-	-	-	37.11
SC-CK-AO-CTR-14		47.6	480	9.8	120	0.58	0.09	6.46	93.45	0.770	1.4604	47.27	285.59
SC-CK-AO-CTR-15		76.7	480	8.7	75	0.93	0.22	4.39	95.39	0.874	1.5325	42.97	186.25

Y=yield; T=temperature; Hr=heating rate; St=soak time at max. temperature; Moisture; A=ash; VM= volatile matter; db=dry basis; FC=fixed carbon; AD=apparent density; RD=real density; P=porosity; IV=iodine value
MW power in case of all experiments = 1200 W

In case of coke obtained from AO pitch (Table 1.7) the physical-chemical characteristics show:

- Coke yield depends on the initial volatile content of the parent pitches. For sample 1 (initial volatile of 68.46 %, Table 1.6) microwave pyrogenation at 450 °C determine about 37 % devolatilization (25 % VM found in sample SC-CK-AO-CTR-10), and a coke yield of 42 wt. % which is considered promising from the point of view of an adequate amount for application. In case of pitch sample 2 (initial volatile of 61.17 %) microwave pyrogenation at 450 °C coke yield accounts an average of 82 wt. % (sample SC-CK-AO-CTR-12 and SC-CK-AO-CTR-13) and average devolatilization of 48 %.
- Fixed carbon has values between 56-74 wt. % in case of green cokes of 450 °C and obviously high values of 93-96 wt. % in case of green cokes of 480 °C.
- Real density accounts values between 1.46-1.53 g cm⁻³ which is in accordance with the type of green coke of 480 °C analysed.
- Opened porosity varies between 40-50 %.
- Iodine value shows different levels, lower in case of non-porous green coke of 450 °C and increased values until 288 mg g⁻¹ for the green coke obtained at 480 °C.

The quality of graphitizable carbon is directly related to its optical texture which is controlled by the development of mesophase during the carbonization process depending on the reactivity of pitch components. The optical texture is defined by the size, shape and orientation of the different mesophase (according to classification systems, all of them similar and based on the same widely used criteria).

Following the experiments and analyses carried out, the microscopical aspects highlight the most representative, original and interesting ones. These are presented qualitatively - as structural type and texture - being correlated with native AO pitch and the technological parameters of microwave heating.

During this treatment the macromolecules formed in the first heat treatment tend to react with each other to form optically anisotropic thermoplastic macromolecular structure, having electric and magnetic properties specific to the liquid crystals. These structures are insoluble in quinoline and the formation of microspheres is visible under the optical microscope with polarized light under

the form of mesophase. High heating rate may cause the mesophase association prior to mesophase grow that happens when heating with low gradients. How textural aspects are associated show an extremely developed optical appearance in agreement with the microwave technology used in this case which cause heating from the inside of the sample. Microscopical analysis carried out on piece samples taken from the core and edge of the coke samples show no difference between the development of the mesophase due to high heating rate and type of the parent AO pitch. The formation and development of optical textures of coalesced mesophase (domains) of large regions are identified in low temperature coke obtained (green coke) from both samples; also, optical textures of mosaics on coarse surface was produced; the decrease in the size of the domains observed for samples processed at lower temperature (450-480 °C) under less severe conditions appear to be related to changes in the molecular structures of the pitch samples.

Coke samples pyrolyzed at 450-480 °C show increased developed optical texture. This seems to indicate that mesophase spherules had enough time to nucleate, grow, and to associate as chains of mesophase spherules that coalesce and grow in highly developed optical textures (Figures 1.11).

The microscopical analysis done, follow the experience proven by the International Committee for Coal and Organic Petrology, Working Group: The Microscopy of Carbon Materials.

The optical texture of the green coke obtained in microwave field at 450 °C show a preferential optical texture of coarse mosaic to domain, and to oriented flow like textures that are larger in size as increase the soak time of coke preparation.

The optical texture of the green coke obtained in microwave field at 480 °C show a more developed texture mostly of flow type and needle like appearance (Figure 1.10). This is a further proof of the fact that the type of heating generated through microwaves straight in the centre of the sample - determines the same chemical transformation as compared to conventional heating by convection slower and of much longer duration and the same morphological and structural changes identified by microscope. Smaller soak times and faster heating rates are the main parameters recommending microwaves as a technology that involves lower consumption of energy compared to the classic one.

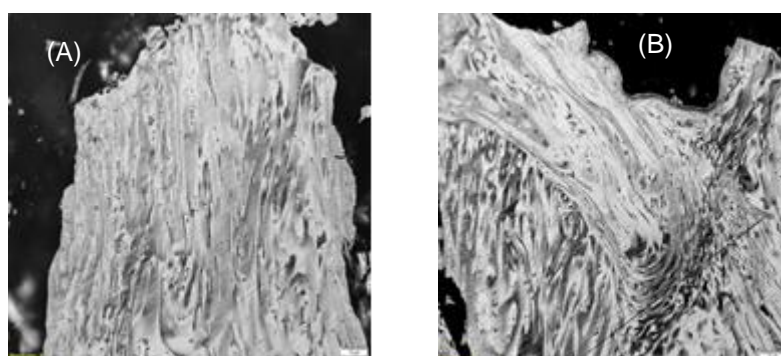


Figure 1.11. Photomicrographs of different optical textures of green coke obtained by microwave heating (obtained from AO pitch precursors, PL, imm, 20X: A) Optical textures of oriented pitch coke of large flow type (450 °C); B) Variety of optical aspects of flow type (480 °C)

Work Package conclusions:

Two industrially scalable processes have been developed to obtain graphene precursors and, in general, advanced carbonaceous materials from two coal-tar fractions; i.e. the raw coal-tar in itself through its distilled pitch after the elimination of impurities (carry-over and metal impurities), and from anthracene oil after oxidative thermal polymerization and distillation obtaining a synthetic pitch.

It is worth highlighting the flexibility of the anthracene oil pitches process to produce precursors of different crystallographic structure, maintaining the structural perfection of graphite. Different crystallographic structures provide different properties that have been evaluated throughout the project; characteristics especially sensitive for the preparation of the subsequent graphene.

Different samples obtained through both processes manufactured by modifying the process variables and initial raw materials were made available to the partner to carry out their project activities.

IQNSA has implemented and scaled the pressurized coking process for the supply of kilogram scale samples to the partners.

On the other hand, also two scalable processes were developed to obtain the pitch cokes: by conventional heating and heated by microwaves. Preparation of low temperature cokes from AO pitch in microwave field represented a novel approach to test the ability of a carbon material precursor as "absorbing material" to enhance the rate of pitch pyrolysis in the microwave field.

Different experimental parameters were tested through both processes to afford the best conditions. A variety of pitch-coke were obtained during a wide range of temperatures varying from low to high: 450-480 °C (green coke), 600-700 °C and 1000-1300 °C, all under N₂ flow.

The pitch cokes were characterized in terms of different typical analysis following the standards used in UPB laboratory.

The step by step processes implemented allowed the preparation of higher amount of precursors of hundreds of grams that have been provided to the partners for advanced analysis, and having adequate properties for the further steps developed throughout the project.

Two devoted microwave heating equipments (experimental and pilot scale) along with associated scalable processes were developed by CTRom assisted by UPB, based on the conventional heating process of low temperature cokes from pitch-like products.

It was observed structural similarities between semi-coke samples made by microwave and conventional heating, for each working temperature, using the optical texture of coalesced mesophase. Also were performed special characterizations for obtained green coke samples.

For green coke production, smaller soak time and faster heating rates are the main parameters recommending microwaves as a technology that involves lower consumption of energy compared to the classic one.

WP2. PREPARATION OF POLYMERIZED ISOTROPIC AND MESOPHASE PITCHES (IQNSA / UPB/ CTRom)

Task 2.1 Preparation of polymerized isotropic pitches (IQNSA)

All samples obtained from the "Reaction Products", were distilled by IQNSA to obtain the corresponding pitches to increase the yield in the eventual coking process. This distillation was carried out in the same Pilot Plant under vacuum conditions (10 mbar).

Due to the similarities of the actions carried out within this task and the next one, the most relevant results of both have been presented in Task 2.2.

All isotropic pitches were manufactured following the same process, i.e. selection of the appropriate precursor (coal-tar without QI or anthracene oil), for the anthracene oil followed by an oxidative thermal polymerization, and additional distillation until reaching the desired softening point.

In this sense, for the isotropic pitch to can be used for the manufacture of carbonaceous materials, the softening point should be higher than 250 °C so that it can be easily thermostated generally using air.

The distillation must be carried out at the lowest possible temperature and with maximum vacuum to inhibit the formation of mesophase. Adequate stirring, and even vigorous, favours this aspect.

Task 2.2 Preparation of mesophase pitches (IQNSA / UPB / CTRom)

The following diagram (Figure 2.1) shows the overall process of the different treatments that IQNSA has made to obtain suitable products for the project.

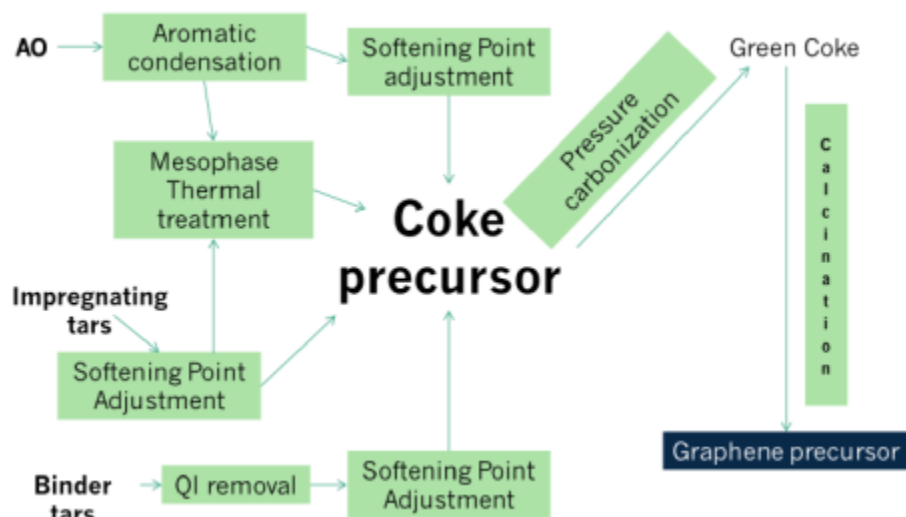


Figure 2.1 Scheme of the overall process followed by IQNSA

From the beginning of the project, IQNSA was aware of the difficulty of carrying out the manufacture of a mesophase pitch according to the current market standards since the softening point increased faster than the mesophase formation. For this purpose, a non-dehydrogenative polymerization process or a catalytic hydrogenation step had to be carried out. Both processes were beyond the scope of the project and the experience and knowledge of IQNSA.

In this sense and given that the objective of these precursors was the manufacture of activated carbons where the softening did not matter, instead of proper mesophase, a coke as green as possible was made for that purpose; that it was totally anisotropic but without yet having the structural and crystalline perfection of a coke. In this way the material would look more like the mesophase than a coke. For this reason, in this report we use the terms green coke or mesophase pitch as a synonymous.

After obtaining a product with an adjusted softening point (coke precursor) the following steps were:

- Intermediate thermal treatment at temperatures around 400-650 °C to produce mesophase / green cokes
- For a mesophase pitch it is important that this preliminary step was performed under nitrogen pressure and with a smooth stirring with the right impeller (confidential information), followed by sudden expansion at the end of the thermal treatment followed

by a soaking time of at least half an hour to eight according with temperature. Temperature should not be higher than 475 °C.

- For cokes, this first step should be also carried out under nitrogen pressure to increase the global yield and temperature needs to be 650 °C to ensure thermosetting of the green coke. Sudden expansion is not necessary.
- For fine mosaics like cokes stirring with the right speed and impeller (confidential information) until the material is almost thermoset is critical
- For needle or large domains like cokes stirring is not as critical but can favour homogeneity. If stirring is selected, it should be very smooth and with the right impeller similar to the mesophase pitch one.
- Additional thermal treatment at temperatures between 1000-1100 °C under atmospheric pressure is required to obtain cokes

During the reporting period the major effort of IQNSA has been focused on the optimization of the equipment required for the realization of the above carbonization under pressure:

- The pressure control loop has been implemented from a manual control to a continuous one, increasing the pressure up to 5 bar. This has allowed introducing pitches of lower softening point that improves the crystallinity of the obtained coke. At the same time, it has allowed scaling-up the process from 0.5 to 5 kg
- The carbonization philosophy has also been implemented, changing from a horizontal to a vertical orientation. This change allows enhancing the crystalline orientation in the vertical direction of the distillation bubbles.
- A scaling-up has been carried out to properly assess the potential industrialization of the project. It has been necessary to carry out a risk assessment study according to the existing regulations with potentially flammable or explosive substances (ATEX).
- The scaling forced to introduce a system of condensation and washing of gases / vapours coming from the furnace.

The pilot plant consists of a Kanthal APM steel tube of 198/182 mm (diam ext / int) and 1000 mm in length, flanged at its ends and using graphite gasket between flanges.

By wrapping the tube, a Fibrothal Half-Cylinder resistor, model HAS 250/750/230, 2 x 4700 W of power is housed. The resistance is fed through a temperature controller that sets the heating ramp according to the pre-set program.

The furnace is placed vertically and held by a metal structure (the vapor washing phase is in blue).

In the lower flange is placed the nitrogen inlet at constant flow through the flow controller FIT-1, an internal temperature meter that will command the temperature controller TIT-1, and the safety relief line through a disk of rupture where a redundant pressure transmitter will be housed.

In the upper flange a relief line will be placed through a safety valve and where a redundant pressure transmitter will be housed and through which the pressure control inside the oven is carried out through the proportional valve V0501. It is the point where the distilled vapors are conducted to Block 3, where they will be cooled and dissolved in the selected solvent. The line that goes from the top flange of the furnace to Block 3 will be thermostat at 150 °C to prevent line blockage by solidification of vapours.

Laterally and at half height a temperature probe will be housed that provides information of the temperature of the exterior wall to the tube to prevent overheating.

In parallel to reach the mesophase formation and evolution the precursor samples were pyrogenated (as a new approach) in a microwave oven by UPB and CTRom. The conditions used for the preparation of the mesophase pitch were: heating rate of 11-12 °C min⁻¹ up to a final temperature of 480 °C and soaking time of 1-2 min. Due to the special conditions of heat generated by the microwave field, the samples for the microscopical characterization were taken from the edge and centre/heart of the semicoke button.

By the petrographic analysis were identified the mesophase formation from the isotropic aromatic parent AO pitch to an anisotropic solid texture (nucleation, coalescing, mesophase coalescing final stage), which reveals the novelty of this research (*Mid Term Report*).

This mesophase ranges from very small embryonic size to larger spheres that gather and coexist with regions of coalesced mesophase (Figure 2.2.).

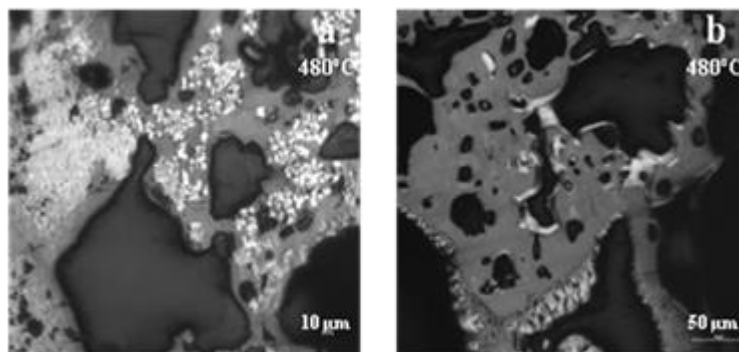


Figure 2.2 Optical micrographs of mesophase in SC-CK-AO-CTR-01(a) spherules (b) coalesced regions

The presence of coalesced regions appears related to the absence of primary QI in this type of pitch, because that AO is obtained as a distillate. Type of mesophase not differs from the well-known mesophase of coal-tar pitch. It was observed that the spherules appear not to have had enough time to nucleate and grow, but to associate as chains of mesophase spherules. Also, to note is that mesophase appears only in samples taken from the centre/heart of coke sample. At the edge of sample any of mesophase spherulites appear.

This agrees with the microwave technology used which cause heating to the inside of the sample and not by classic heat transfer from outside to inside. High heating rate may cause the mesophase association prior to mesophase growth that happens when heating with low gradients.

Also, a few optical types looking very similar to pyrocarbon were observed. Knowing that the formation of pyrocarbon is related to high temperatures (over 900 °C) we may assume that the reaction kinetics was shifted into direction of new chemical reactions which could generate exothermic reactions.

Task 2.3 Characterization of carbon materials precursors (IQNSA / UPB)

To produce the mesophase pitches or green cokes, IQNSA used the same AO pitch SC-PT-AO-QN-01 with further thermal treatment.

The resultant green cokes (SC-CK-AO-QN-02, SC-CK-AO-QN-09 and SC-CK-AO-QN-10) were characterized by optical microscopy to see the mesophase extension (Figure 2.3).

In samples SC-CK-AO-QN-02 and SC-CK-AO-10 a completely anisotropic structure was formed and just traces of an isotropic phase could be found. On the other hand, in sample SC-AO-QN-09 can be observed perfectly how mesophase spheres are formed from the isotropic phase (Figure 2.3 (b)) to finally occlude forming the anisotropic phase (Figure 2.3 (c)).

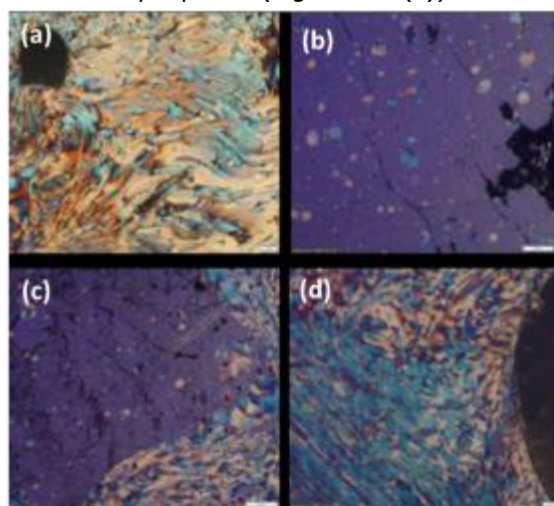


Figure 2.3 Optical micrographs of the green cokes (a) SC-CK-AO-QN-02 (b, c) SC-CK-AO-QN-09 (d) SC-CK-AO-QN-10

The characterization of the different polymerized isotropic pitches obtained was carried out by standard procedures (proximate analysis, solubility parameters, softening point). The results have been detailed in the *Second Annual Report*. Table 2.1 and Table 2.2 summarizes the most representative ones, as the pitches shown were subsequently used by INCAR-CSIC as precursors for the synthesis of ACs and graphene materials.

Table 2.1 Anthracene oil (AO) polymerization in microwave semi-pilot equipment and main characteristics of the pitch-like products

Samples ID	Proximate analysis wt. %		Ultimate analysis wt. %				TI wt. %	QI wt. %	SP (RB/M) °C
	Volatile db	FC	C	H	N	O			
SC-PT-AO-CTR-18	71.8	28.2	91.4	4.8	1.3	2.5	17.6	0	71
SC-PT-AO-CTR-19	66.9	33.1	91.5	5.0	1.5	2.0	14.0	0.2	89/95
SC-PT-AO-CTR-20	38.4	61.6	88.8	4.0	1.4	5.8	60.7	24.4	221

Table 2.2 Main characteristics of the AO pitch samples

Sample ID	Yield wt. %	VM^{db} wt. %	FC wt. %	SP (Mettler) °C	TI wt. %	QI wt. %
SC-PT-AO-CTR-31	40.8	68.46	31.54	91.1	17.78	<0.2
SC-PT-AO-CTR-32	32.5	61.17	38.83	111.7	24.44	<0.2

The formation of anisotropic mesophase pitches from the isotropic phase during heating and the structural organization before and after solidification to low temperature coke was identified. The optical texture was defined by the size, shape, and orientation of the different mesophase spheres corresponding to different pyrogenation stages. The morphological differences between the sample precursors type, the influence of heating rate within the temperature interval (which will ensure a certain range of physical properties of the products) was also evaluated.

Work Package conclusions:

During the project, the procedure for the manufacture of isotropic and mesophase pitches from coal-tar fractions has been developed.

Pilot plants for manufacturing anthracene oil pitch, eliminating coal-tar QI and distilling the resultant products up to the desired softening point all of them at a capacity of kg h⁻¹, were put at the service of the project for the manufacture of samples precursors for the different target materials of the project; isotropic and mesophase, as well as different cokes from needle to fine mosaics.

Additionally, IQNSA scaled-up and implemented an existing tubular furnace in its facilities, to be able to operate up to 5 kg per batch under ATEX safety conditions, and thus to be able to manufacture large quantities of mesophase pitch and cokes with needle, large domains or fines mosaics structure.

All the precursor and raw material for the specific target carbon material for the project were submitted to the rest of the partners and characterized from both sides INCAR-CSIC and IQNSA.

In parallel interesting results were obtained by CTRom and UPB by studying the microwave heating technology effects (in terms of heating rate, final temperature and soaking time) on the development of mesophase. The results showed that microwave energy was led directly to the material through molecular interactions with the electromagnetic waves being transformed into heat inside the particles by dipole rotation and ionic conduction.

The characterization of the representative polymerized isotropic pitches obtained was carried out by standard procedures (proximate analysis, solubility parameters, softening point). The results showed the most representative ones that were used by INCAR-CSIC as precursors for the synthesis of ACs and graphene materials.

It was developed a microwave assisted synthesis strategy for obtaining isotropic and mesophase pitches from coal-tar fractions. A high heating rate and reduced soaking time related to microwave heating are principal operating parameters.

WP3. SYNTHESIS AND CHARACTERIZATION OF ACTIVATED CARBONS (ACs) (UPB / CTRom / TUWRO)

Task 3.1 Influence of the selection of carbon precursors (polymerized isotropic/mesophase pitches and low temperature cokes) and activation procedures on the activated carbons characteristics (UPB / CTRom)

The work carried out was mainly aimed at defining the conditions of AO processing as precursor of carbon materials. Consequently, they gave rise to documentation, in the present state of knowledge, for defining the experimental frame for the subsequent applications, in terms of using microwave heat technology for the studied processes. Starting from the very first stage of the project, the realization of equipment for classical/conventional heat treatment, specific for the requirements of the foreseen activities, was justified by the following reasons:

- High degree of novelty of microwave heating technology applied to the treatment of coal-liquid based carbon precursors.
- Choosing of one single functional model, where both thermal processes can be achieved (Pyrogenation at temperatures of 480 - 700, 850 and 1000 °C as well as activation at 1000 °C).

UPB considered mandatory to study phenomena transformation under conditions of conventional heat treatment (electrical resistance strictly thermostatically controlled). Follow the working parameters thus set up, will allow the design and construction of the equipment for the microwave field. So, the following activities were drawn:

- Identification and characterization of the conventional heating laboratory equipment: profile and capacity, raw material and end product, functional and technological description of the installation, process flow sheet main items.
- The main scheme for the laboratory module execution is based mainly on the documentation given by the international standard ISO 18894 "Coke-Determination of coke reactivity index (CRI) and coke strength after reaction (CSR)" developed in 2006, starting from the principle of similarity processes of coke gasification and char activation with CO₂.
- Description of the main constructive requests for technological assembling and process design: design scheme, working conditions, constructive and functional specificity of the equipment.

Moreover, design data of the equipment and calculation of heat transfer through the oven walls for two constructive variants of the oven were presented.

- The programming and control system were finalized during first half of 2016 after completion of the oven which was optimally adapted to specific operating conditions.
- The testing of the installation was carried out under the conditions of assembling in the heating oven with empty metallic retort, and heated to 1000 °C, with air inlet.
- The equipment was used to perform all the coking (Appendix 4, available on CIRCABC) and activation (Appendix 6, available on CIRCABC) tests.

The technical documentation - technological solutions - and the process details designs SCP 001 (16 drawings) and SCP 004 (5 drawings) were elaborated and are enclosed in the *Mid-Term Report*. The elaborated execution documentation was provided to CTRom with the address no. 529/15.10.2015. and UPB gave technical assistance during the entire period of execution. UPB assisted CTRom during the realization of the spare parts of the equipment, starting-up and experimental tests.

As stated, the temperature to obtain the carbon precursor influences the adsorption of the AC capacity expressed by the iodine value and S_{BET} . Both parameters decrease when increasing temperature from that of the green coke (480-500 °C) to the high coke temperature (over 900°C).

Green coke (up to 500 °C) is suitable for chemical activation obtaining a iodine value over 1000 mg g⁻¹ and a surface area, S_{BET} , over 800 m² g⁻¹.

Chemical activation using microwave heating of AO and pitch cokes show that the iodine value and S_{BET} increase as the soak time at max. temperature increasing from 10, 20 and 30 minutes.

Chemical activation at 700-800 °C produces typical changes for this type of material: extension of pores with weight loss increasing starting with the ultra-microporosity, which is gradually transformed in micropores and then in mesopores. The optical microstructural studies on the activated carbon, intend to reveal the different appearance of textures in chemical activation.

The original character of the research is emphasized by the attempt to correlate different type of carbon textural aspects with their higher or smaller susceptibility and/or selectivity, versus the activating agent. The photomicrographs of the activated carbons show characteristic images for the degassing evolution stages during the chemical activation progress. Depending on carbon type (green coke or high temperature coke) they reveal the decreasing of porosity up to a certain limit.

After that, the progressive weight loss of carbon substance takes place which lead to the pores enlargement and the decreasing of the adsorption surface.

These experiments are preliminary, prospective, being conducted in laboratory conditions other than those that we have proposed. This is because only in the next stage, after CTRom will start-up the equipments specified in the project we can achieve the parameters that we have proposed (*Second Annual Report*).

Chemical activation is an efficient and relatively simple process. Chemically activated carbons are produced by mixing an activation chemical agent (in our case KOH) with carbon precursor (green coke) and carbonizing the resultant mixture. The carbonization temperature is relatively low, around 700 °C.

In case of chemical activation of smaller amounts of sample UPB manually mixed the green coke and the activating agent (KOH) in an Agatha mortar (instead of the more appropriate ball-mill) (see Mid-term and Second Annual Reports).

In case of chemical activation of higher amounts of sample UPB overcome these problems by mixing higher amount of carbon precursors and KOH in a ball-mill in order to produce a more intimate contact between the green coke and the activating agent.

So that, in 2018 UPB purchased some accessories to increase the performance of the existing laboratory mill and performed the sample preparation in a more adequate way, Figure 3.1.

The UPB laboratory procedure was presented in detail in *Mid-term Report, Deliverable D 3.1*.

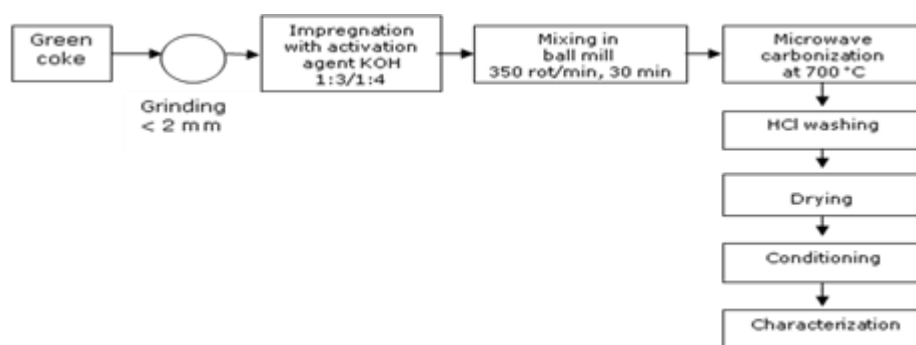


Figure 3.1 Basic flow sheet of chemical activation performed by microwave heating

Seven (7) experiments of chemical activation with heating in a microwave field (equipment no.6, Figure 1.10) were carried out, the respective samples of activated carbon being supplied to INCAR for further characterization.

The details of operating parameters and characteristics of the activated carbons obtained appear in Deliverable 3.2 (Report on the ACs standard characteristics) of this Final Report.

Method: The alumina crucible is put inside of the microwave applicator, put the special lid on the applicator, and insert the k-thermocouple inside of the crucible. It sets-up the working temperature on the thermal-controller. Start the ventilation hood. Start the microwave generator and monitoring the temperature. The microwave power can be adjusted using a power auto-transformator, to control the heating thermal gradient. When is reached the working temperature, the controller will maintain the constant temperature using a predefined algorithm. After finishing the thermal program, the crucible will be kept inside of the applicator until the temperature will decreased at a safety operational level. Then the crucible with obtained activated coke will be weighed to establish the conversion level.

Parameters investigated were: type of heating (microwave); quality of the raw material (AO pitch coke) and temperature of carbonization (450 and 480 °C); activation temperature (700 °C); duration of the activation/soak at the maximum temperature (1 to 2 hours); green coke:KOH ratio (1:3 and 1:4). In all experiments were used an amount of 40 g of green coke. In 2018 UPB purchased some accessories to increase the performance of the existing laboratory mill and performed the sample preparation in a more adequate way.

Simulation of electromagnetic field:

For the study of a microwave irradiation system, using the QW-Modelator program for QuickWave, was drawn the pilot scale microwave assisted equipment no. 6 for producing of activated carbon, in the following sequence: a cylindrical cavity containing in the XY plane one WR340 waveguide, a alumina cylindrical crucible and a dielectric material as a mixture between potassium hydroxide and green coke. The calculation of the describing parameters of the mixture was performed using a linear combination of the parameters of the individual components according to the mass weights in which they are found in the mixture.

In Figure 3.2 is a drawing of the assembly of the enclosure and the magnetron

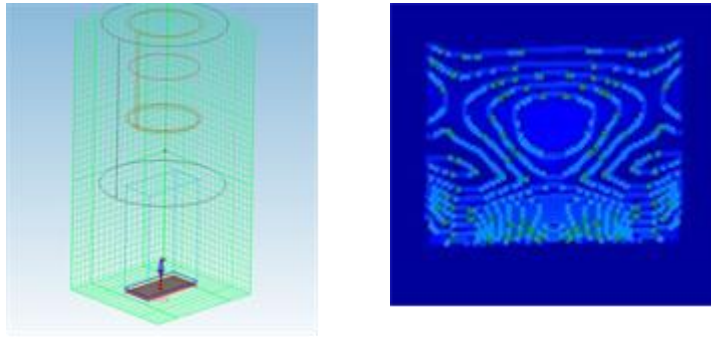


Figure 3.2 (Left) Axonometric drawing of the pilot scale equipment microwave assisted for producing the activated carbon. (Right) The thermal field inside in the dielectric material

To simulate the room irradiation process, the time domain type solver from the QuickWave2016 package was used. Simulator setting parameters were: Frequency: 2.46 GHz; Frequency range: 2.2 to 2.6 GHz; Generation mode: TE10; Number of generating ports: 1; Microwave power: 1200 W; Waveguide type: WR-341; Waveguide Layout Plan: XOY; Injection chamber: cylindrical.

The electromagnetic field for the generation system called the port was simulated. A simulation package filter was performed to observe the distribution of the electric field, which is a heating generator in contact with a material that presents its own dipole or induced momentum. Figure 3.3 shows the thermal field distribution in dielectric material. Microwave heating of samples for chemical activation was carried out following the following procedure:

- From room temperature up to KOH melting point was used 400 kW microwave power energy to realize a thermal equilibrium in alumina crucible; this was done in order to reduce the risk of crucible damage.
- From KOH melting point up to soak temperature was used 1200 kW microwave power energy to assure the necessary energy for sample heating.

Based on numerical simulations, the following were obtained:

- The cutting frequency for the hollow cylindrical cavity has the value of 1.6989 GHz;
- The quality factor Q_e for the hollow cylindrical cavity has the value of 2905.6;
- The quality factor Q_e for the dense region (KOH-green coke mixture) has the value of 2268.5;
- Dissipated power for the dense region (KOH-green coke mixture) has the maxim value of 1198 W and the mean value of 902 W
- For this application, in order to avoid the thermal energy accumulation on the right-angled bottom of the cylindrical crucible, was chosen an A type crucible with rounded bottom.

With QW-Modelator program for QuickWave, was drawn the pilot scale equipment microwave assisted for producing of activated carbon, in order to simulate electromagnetic field influence on KOH: green coke mixture:

- the cutting frequency for the hollow cylindrical cavity has the value of 1.6989 GHz;
- the quality factor, Q_e , for the hollow cylindrical cavity has the value of 2905.6;
- the quality factor, Q_e , for the dense region (KOH-green coke mixture) has the value of 2268.5;
- dissipated power for the dense region (KOH-green coke mixture) has the maxim value of 1198 W and the mean value of 902 W
- for this application, in order to avoid the thermal energy accumulation on the right-angled bottom of the cylindrical crucible, was chosen an A type crucible with rounded bottom.

Seven (7) experiments of chemical activation with heating in a microwave field were carried out, the respective samples of activated carbon being supplied to INCAR for further characterization, Table 3.1.

The details on operating parameters and characteristics of the activated carbons obtained appear in Deliverable 3.2 (Report on the ACs standard characteristics) of this Final Report.

The parameters investigated were: type of heating (microwave); quality of the raw material (AO pitch coke) and temperature of carbonization (450 and 480 °C); activation temperature (700 °C); duration of the activation/soak at the maximum temperature (1 to 2 hours); green coke:KOH ratio (1:3 and 1:4). In all experiments were used an amount of 40 g of green coke.

The mechanisms of higher ratio of solid KOH interaction with the surface of green coke at 700 °C is detailed within Deliverable 3.2.

These experiments were conducted in pilot conditions same that we have proposed. In parallel, INCAR-CSIC has characterized the AC in a more complex way.

On carbonization, the chemical acts as a support, and does not allow the resulting char to shrink. The result is a very porous carbon structure, filled with activation agent.

This process produces activated carbons with large pores, although the pore size distribution is determined for a given raw material mainly by the degree of impregnation (the larger the degree of impregnation, the larger is the pore size of the final carbon).

Table 3.1 Preparation of activated carbon in microwave field - parameters and characteristics

AC sample ID	Parent coke ID	Activation characteristics					Activated carbon characteristics						
		Ratio C:KOH	Y wt. %	T °C	Hr °Cmin ⁻¹	St min	Proximate analysis			Porosimetric analysis			
							A ^{db} wt. %	VM ^{db} wt. %	FC wt. %	IV mgg ⁻¹	S _{BET} m ² g ⁻¹	Total pore volume cm ³ g ⁻¹	Pore average radius, Å
SC-AC-CTR-07	SC-CK-CTR-10	1:4	87.15	700	10	60	0.4	11.2	88.4	1225.9	2205	0.20	21.48
SC-AC-CTR-08	SC-CK-CTR-11	1:3	82.4	700	8.5	60	2.2	5.6	92.2	1224.5	2022	0.18	14.84
SC-AC-CTR-09	SC-CK-CTR-12	1:3	46.3	700	7.5	60	1.5	3.9	94.5	1173.9	1123	0.05	19.64
SC-AC-CTR-10	SC-CK-CTR-13	1:4	88.9	700	10	60	0.7	12.5	86.8	1220.2	2069	0.15	20.23
SC-AC-CTR-11	SC-CK-CTR-14	1:3	90.2	700	6.0	60	1.1	6.9	92.0	1174.8	1086	0.04	15.16
SC-AC-CTR-12	SC-CK-CTR-15	1:3	88.7	700	5.9	60	1.3	5.8	92.9	1209.2	1437	0.10	16.54
SC-AC-CTR-13	SC-CK-CTR-15	1:3	91.3	700	13.5	120	1.5	16.6	81.9	912.1	600	0.01	16.00

Y=yield; T=temperature; Hr=heating rate; St=soak time at max. temperature; Moisture; A=ash; MV= volatile matter; db=dry basis; FC=fixed carbon; AD=apparent density; RD=real density; P=porosity; IV=iodine value MW power in case of all experiments = 1200 W

All synthesis were performed under N₂, flow rate of 1.2 Lmin⁻¹

In parallel, INCAR-CSIC synthesized four ACs by chemical activation (with KOH) and the subsequent conventional heating of both, the "Green cokes" provided by IQNSA (SC-CK-AO-QN-02, SC-CK-AO-QN-09 and SC-CK-AO-QN-10) and a green coke derived from a microwave pitch (Task 1.4). Even though it was not an INCAR-CSIC task but considering its wide experience in the production of this kind of carbon materials, this option was considered in order to compare the ACs thus obtained (SC-AC-02, SC-AC-09, SC-AC-10 and SC-AC-11) with those obtained by UPB (previously described).

Task 3.2 Preliminary characterization of the activated carbons synthesized (UPB)

Characteristics of the activated carbons were detailed in Deliverable D 3.1. Report on the Activation technology performance enclosed in the MidTerm Report.

According to the results obtained in the preliminary phased of the research, the ratio between green coke:KOH was increased to obtain a higher surface area of the carbon precursor. This produced an increase in the adsorption capacity of the resulting AC according to the iodine value and S_{BET}. Green coke (of 450 °C) is suitable for chemical activation obtaining a iodine value over 1220 mg g⁻¹ and a surface area, S_{BET}, over 2200 m² g⁻¹, Table 3.1. The reason is that the

interaction of KOH is more effective in coke of 450 °C, less carbonized compared to that of 480 °C, which has an increased carbon structural organization and thus, is more resistant to attack by KOH.

The S_{BET} values show an important variation (Figure 3.3): in sample SC-AC-AO-CTR-07 the S_{BET} value is with 272 % higher than in the sample SC-AC-AO-CTR-13.

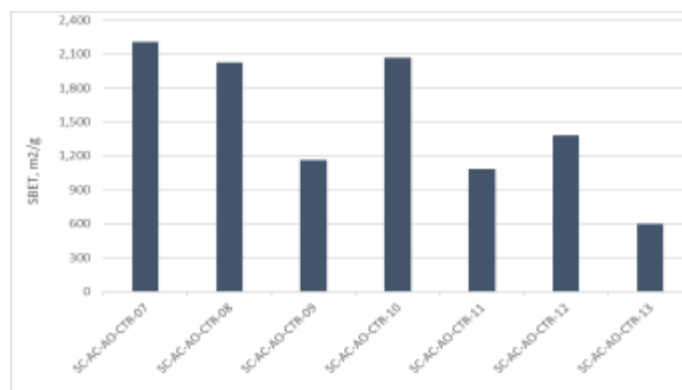


Figure 3.3 S_{BET} variations for analysed samples

The total pore volume is higher for samples SC-AC-AO-CTR-07 and SC-AC-AO-CTR-08 corresponding to the parent pitch sample#1, while the pore average radius is the highest for sample SC-AC-AO-CTR-07, followed by those in samples SC-AC-AO-CTR-10 and SC-AC-AO-CTR-09 (Figure 3.4).

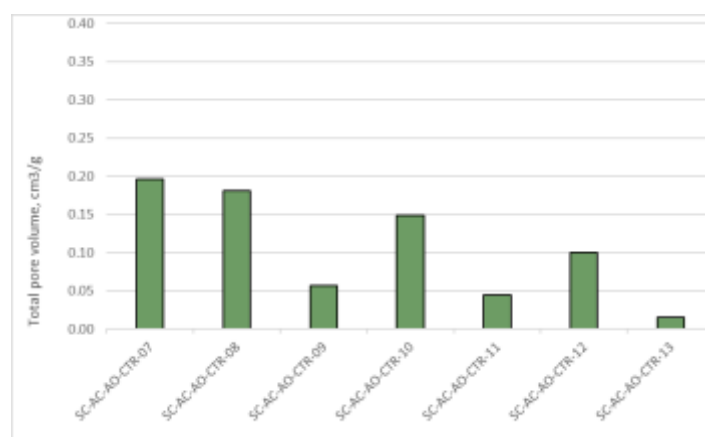


Figure 3.4 Total pore volume variations for analysed samples

The aspect of microphotographs is somewhat similar in both pitches of sample 1 and 2. Chemical activation at 700 °C produces typical changes for this type of material: extension of pores with weight loss increasing starting with the ultra-microporosity, which is gradually transformed in micropores. Chemical activation using microwave heating of AO pitch green cokes show that the S_{BET} does not increase as the soak time at max. temperature increased from 1 to 2 hours. From the porosimetric analysis for all samples analyzed an average pore radius between 14-20 Å results which show large volume of AC micropores.

The optical microstructural studies on the activated carbon, reveal the different appearance of textures in chemical activation, Figure 3.5.

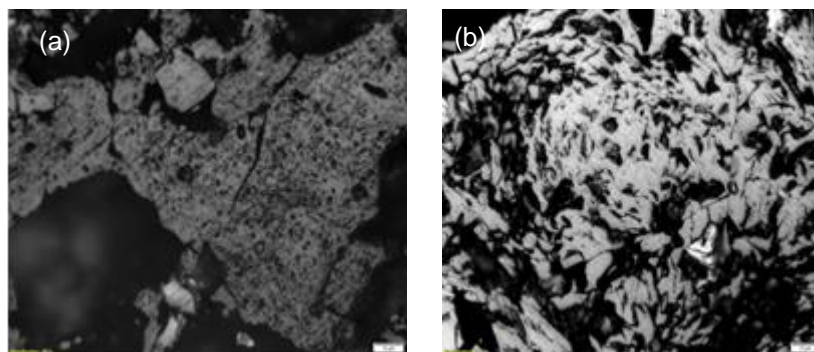


Figure 3.5 Aspects of developed micro-porous structure in AC originating from AO green coke of 450 °C (a) and 480 °C (b).

The microscopic analysis in case of AC derived from 450 °C green coke show a structure with an increased microporosity (Figure 3.4.a) while in the case of AC derived from 480 °C green coke is somewhat obvious in case of wider micro-pores (Figure 3.4.b). The original character of the research is emphasized by the attempt to correlate different type of carbon textural aspects with their higher or smaller susceptibility and/or selectivity, versus the activating agent. The photomicrographs of the activated carbons show characteristic images for the degassing evolution stages during the chemical activation progress. Depending on carbon type (green coke) they reveal the decreasing of porosity up to a certain limit. After that, the progressive weight loss of carbon substance takes place which lead to the pores enlargement and the decreasing of the adsorption surface.

Details are enclosed in the Deliverable 3.2 (Report on the ACs standard characteristics) of this Final Report.

With comparative purposes, INCAR-CSIC has included, as a preliminary characterization, the characteristics of the different ACs obtained inside Task 3.2 (Table 3.2). The advanced characterization of these samples, carried out by UEA, has been included in Task 7.1.

Table 3.2 Characteristics of the ACs obtained by chemical activation/conventional heating of low temperature cokes derived from conventional and microwave pitches

Sample	S_{BET} ($m^2 g^{-1}$)	V_T^* ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{meso} ($cm^3 g^{-1}$)	O (wt. %)
SC-AC-02	1402	0.62	0.49	0.13	6.6
SC-AC-09	2306	1.01	0.80	0.21	5.8
SC-AC-10	2630	1.15	0.90	0.25	8.0
SC-AC-11	2830	1.26	0.92	0.34	5.9

According to the data this SC-AC-11, from a microwave derived precursor, shows a higher specific surface area and better textural properties than the previously obtained from conventional derived precursors. This good result presents the microwave technology as a promising route in order to obtain new carbon precursors which will lead to activated carbons with comparable or improved properties when comparing with the traditional ones.

Task 3.3 Activated carbons with different oxygen functional groups distribution (TUWRO)

Activated carbons (ACs) are widely used as electrode materials for supercapacitors due to their high specific surface area, the ease of pore size distribution tailoring, relatively good electrical conductivity, high chemical stability, availability and low cost. The commercial electrochemical capacitors are based on the electrostatic charge accumulation at the electrode/electrolyte interface (electric double-layer capacitors EDLCs), which is related to the surface accessible to the electrolyte ions. It is proved that the capacitance is proportional to the specific surface area of the carbon material [1]. However, the development of the carbon surface above $2500 m^2 g^{-1}$ is unsuitable for application in EDLCs [2]. Generally, the capacitance of ACs does not exceed $250 F g^{-1}$. It is possible to develop an electrode material with higher capacitance value if metal oxides (e.g. MnO_2) and conducting polymers (e.g. polyaniline) are used for this purpose due to their very high pseudocapacitance. An increase in the capacitance of carbon materials can be achieved by introducing the oxygen and nitrogen groups on the carbon structure [3,4]. This is because some

types of oxygen and nitrogen functional groups may provide redox activity to develop the pseudocapacitance, leading to an increase of the overall capacitance [5].

The objective of Task 3.3 was to introduce the oxygen groups into the surface structure of ACs. Considering that the larger the specific surface area, the higher is the capacitance value, the preservation of the surface area of the initial AC during its modification is highly desirable.

Different oxidative approaches were applied as follows: i) wet oxidation using a mixture of nitric acid and sulfuric acid, and ammonium persulfate, ii) dry oxidation with air and iii) electrochemical oxidation. The ACs (SC-AC-02, SC-AC-09, SC-AC-10, SC-AC-11) were provided by INCAR for this study. Additionally, a microwave-assisted anthracene oil-based pitch (P27) was provided by UPB/CTRom and used for the preparation of AC by KOH activation in TUWRO.

Preparation of P27-AC: First, P29 pitch was pyrolyzed in a retort-type reactor under stirring at 520 °C with a temperature ramp of 5 °C min⁻¹ and soaking time of 2 h. The residue obtained was heat-treated in a quartz boat at 650 °C for 1 h under nitrogen to remove the rest of volatile matter and increase slightly the carbon structure ordering. The coke was activated with KOH at mass ratio of 1:3 at 800°C for 1 h. The product was washed with HCl solution, boiled distilled water, filtered and dried at 110 °C for 8 h. AC is labelled P27-AC/800-3.

Acid treatment: The oxidation of SC-AC-02 was carried out at room temperature for 1 h using a mixture of 19 % HNO₃ and 96 % H₂SO₄ in the ratio of 1:3 (v/v). Due to higher reactivity, SC-AC-09 was treated with a mixture of 10 % HNO₃ and 48 % H₂SO₄ in the ratio of 1:3 (v/v). After the oxidative treatment, the oxidized samples were washed with distilled water to neutral pH, filtered and dried at 110 °C for 8 h. NS corresponds to oxidative treatment with an acid mixture.

Ammonium persulfate oxidation: The oxidation of SC-AC-09 was performed at room temperature using concentrated (NH₄)₂S₂O₈ (AP) and a mixture of water/(NH₄)₂S₂O₈ (1:1 v/v) (AP 1:1). The time of oxidative treatment ranged from 1 to 24 h. Afterwards, the oxidized samples were washed with boiled distilled water, filtered and dried at 110 °C for 8 h. The labelling of the samples treated with ammonium persulfate is as follows: AC name/time of oxidation AP (AP 1:1).

Air treatment: A sample of AC was placed as a thin layer at the bottom of a quartz boat, which was then inserted in a horizontal reactor. The reactor was heated to a desired temperature at a heating rate of 5 °C min⁻¹ in an inert atmosphere and subsequently, air (12 L h⁻¹) was introduced into the reactor. After treatment with air, the reactor was cooled to room temperature under a nitrogen flow. The oxidative treatment was performed at different temperatures in the range of 250-400 °C for 0.5-2 h min depending on the modified AC. The labelling of the samples treated with air is as follows: AC name - temperature of oxidation/time of oxidation air.

Electrochemical oxidation: The approach was based on anodic oxidation of the AC suspension in 0.5 M Na₂SO₄ inside a platinum crucible polarized at 0.3 V (named as "mild oxidation", EOX1) and 0.7 V ("moderate oxidation", EOX2) vs. Hg|Hg₂SO₄ reference electrode for 18 h.

The oxidized samples were characterized by elemental analysis (EuroVector model 3018) and N₂ sorption at -196.1 °C (Autosorb IQ, Quantachrome) to monitor the changes in the oxygen content and the textural parameters such as the BET surface area (S_{BET}), the total pore volume V_T, the micro- and mesopore volumes (V_{micro} and V_{meso}) and the average micropore width (L₀). The Quenched-Solid Density Functional Theory (QSDFT) [6] analysis was applied to the N₂ adsorption isotherms to determine pore size distribution (PSD). Figure 3.6 shows the nitrogen sorption isotherms and the pore size distribution for the selected series of oxidized SC-AC-02 (a, b), SC-AC-09 (c, d), SC-AC-10 (e, f) and SC-AC-11 (g, h). All isotherms are of type I according to the BDDT classification, indicating the microporous nature of the studied ACs.

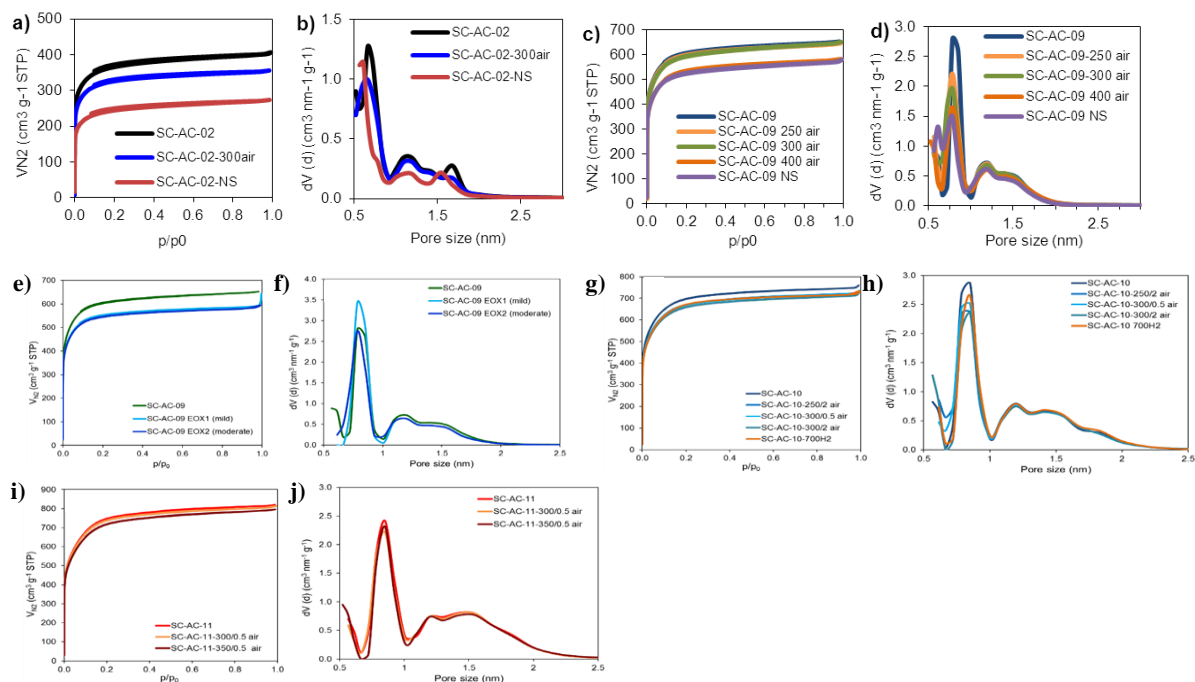


Figure 3.6 Adsorption-desorption isotherms of N_2 at $-196.1\text{ }^{\circ}\text{C}$ and the pore size distribution of the oxidized ACs. (a, b) SC-AC-02, (c - f) SC-AC-09, (g, h) SC-AC-10 and (i, j) SC-AC-11.

Table 3.3 depicts the loss of weight on oxidative treatment, the oxygen content (dry sample) and the textural parameters of the oxidized ACs. The monitoring of the loss of weight induced by oxidation allowed optimizing the conditions of the oxidative treatment. An excess of weight loss indicates a drop of the porosity development which is undesirable.

Table 3.3 Characteristics of the ACs oxidized by different methods.

Sample	Loss of weight (%)	Oxygen content (wt. %)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_T ($\text{cm}^3 \text{g}^{-1}$)	V_{DR} ($\text{cm}^3 \text{g}^{-1}$)	V_{DR}/V_T	L_0 (nm)
SC-AC-02	-	6.6	1402	0.62	0.49	0.79	0.91
SC-AC-02-300/0.5 air	7.1	7.3	1261	0.55	0.44	0.80	0.89
SC-AC-02-NS	8.2*	17.9	919	0.42	0.34	0.81	0.91
SC-AC-09	-	5.9	2306	1.01	0.80	0.79	1.14
SC-AC-09-250/0.5 air	2.8	6.4	2296	1.00	0.78	0.78	1.06
SC-AC-09-300/0.5 air	4.4	7.0	2258	1.00	0.78	0.78	1.09
SC-AC-09-400/0.5 air	4.5	10.0	2024	0.90	0.69	0.77	1.08
SC-AC-09-NS	0.3	13.5	1999	0.89	0.69	0.79	1.03
SC-AC-09-EOX1	n.d.	8.4	2100	0.95	0.76	0.80	1.21
SC-AC-09-EOX2	n.d.	10.1	2090	0.92	0.75	0.82	1.24
SC-AC-09/1 AP	n.d.	21.1	1960	0.86	0.68	0.79	1.03
SC-AC-09/24 AP	n.d.	29.7	1560	0.69	0.55	0.79	1.00
SC-AC-09/1 AP 1:1	n.d.	17.8	1950	0.86	0.68	0.79	1.04
SC-AC-10	-	8.0	2630	1.15	0.90	0.79	1.25
SC-AC-10-250/2 air	7.2	8.7	2520	1.12	0.86	0.77	1.23
SC-AC-10-300/0.5 air	6.7	7.8	2530	1.12	0.86	0.77	1.23
SC-AC-10-300/2 air	7.8	9.4	2480	1.08	0.84	0.78	1.21
SC-AC-10-700 H_2	18.3	2.0	2520	1.12	0.85	0.76	1.28
SC-AC-11	-	5.9	2830	1.26	0.92	0.73	1.33
SC-AC-11-300/0.5 air	5.2	6.5	2780	1.25	0.91	0.73	1.31
SC-AC-11-300/2 air	6.1	7.8	2662	1.22	0.87	0.72	1.28
SC-AC-11-350/0.5 air	6.6	7.7	2710	1.23	0.88	0.72	1.32
P27-AC/800-3	-	4.2	2020	0.91	0.70	0.77	1.06
P27-AC/800-3-300/2 air	5.5	7.1	1790	0.82	0.62	0.76	1.09

* increase of the sample mass

For all ACs, the oxygen content increases after oxidative treatment applied using different oxidants. The wet oxidation is more efficient for oxygen incorporation into the structure of carbon surface than the dry oxidation. ACs treated with a mixture of acids or ammonium persulfate contain as high as 17.9-29.7 wt. % of oxygen. However, these modifications lead to reduction in the porosity development of the starting AC to a high extent. A large drop of the BET surface area,

from 2306 to 1560 m²g⁻¹ was observed due to wet oxidation of SC-AC-09. This makes the wet oxidation unsuitable as a method for introducing the oxygen functionalities on the carbon surface for the electrochemical purposes. The oxidation of AC with air appeared to be more promising. As expected, with increasing temperature or time of oxidation, the oxygen content increases in the oxidized ACs. For instance, an increase in the temperature from 250 to 400 °C results in an increase in the oxygen content from 5.9 to 10.0 wt. % for SC-AC-09 treated with air for 0.5 h. With increasing oxidation time from 0.5 to 2 h at 300 °C, an increase in the oxygen content from 7.8 to 9.4 wt. % was observed for SC-AC-10. Unfortunately, enrichment in the oxygen is followed by a decrease in the BET surface area, however, to much lower extent compared with wet oxidation. For instance, the oxidation of SC-AC-09 at 300 °C for 0.5 h leads to an enhanced oxygen content (5.9 vs. 7.0 wt. %), which is accompanied by a 2 % decrease of S_{BET} only. The same trend was revealed for SC-AC-11. A higher decrease in the BET surface area is observed when AC (SC-AC-09) was electrochemically oxidized. An increase in the oxygen content up to 10.1 wt. % is followed by about 10 % reduction of S_{BET}.

P27-AC/800-3 is characterized by the lowest oxygen content among the studied ACs (4.2 vs. 5.9-8.0 wt. %) which would suggest its better conductive properties. The treatment of this AC with air at 300 °C for 2 h leads to a high enrichment in oxygen (7.1 wt. %), but approximately 11 % loss of specific surface area is followed.

In order to evaluate the impact of oxygen on the electrochemical behavior of AC, SC-AC-10 was subjected to hydrogen treatment at 700 °C for 2 h in order to remove less stable oxygen functional groups. As a result, a four-fold decrease in the oxygen content was achieved, from 8.0 to 2.0 wt. %.

The oxidative treatment causes not only a decrease in the surface area but also results in a decrease in the micropore and mesopore volumes. Except for electrochemical oxidation, worsening porosity development is followed by slight narrowing of the micropore size. As can be seen in Fig. 3.3.X1 the shape of the pore size distribution (PSD) profile of the initial AC is preserved after its oxidative treatment. Four maxima can be distinguished in the PSD profiles. The main maximum occurs at ~0.8 nm and the others less intensive are observed at ~1.2, 1.4 and 1.8 nm. The most distinct changes are observed in the intensity of the maximum at ~0.8 nm which decreases with the oxidation degree of AC. A different porosity development is observed for electrochemically oxidized ACs. Their average micropore size is higher than that of the initial AC (SC-AC-09) and the contribution of micropores with a size of 0.72-0.83 nm is higher in case of mild oxidized AC (SC-AC-09-EOX1) compared with SC-AC-09.

Different oxidative treatments applied, using different oxidants and processes parameters, have provided a series of ACs with different oxygen functional groups distribution. Surface chemistry of the oxidized ACs was characterized by XPS (WP7, EUA).

Task 3.4 Activated carbons with different N-containing functional groups distribution (TUWRO)

The objective of Task 3.4 was to introduce nitrogen functional groups on the activated carbon surface. Similarly, to oxygen functional groups, some nitrogen functionalities contribute in the enhancement of the capacitive behavior of ACs. Pyridinic, pyrrolic/pyridonic and pyridine-oxide groups are responsible for increasing the overall capacitance through reversible redox reactions, whereas quaternary nitrogen improves the conductivity of the electrode material [7]. Moreover, the introduction of nitrogen groups on the carbon surface enhances its wettability which is very important for the performance of supercapacitors operating in aqueous electrolytes.

The nitrogen functional groups were introduced on the AC surface applying three approaches as follows: i) treatment with gaseous ammonia at high temperature (amination), ii) treatment with ammonia at low temperature under hydrothermal conditions and iii) heat treatment with urea. Four AC samples (SC-AC-02, SC-AC-09, SC-AC-10, SC-AC-11 and P29-AC) were the subject of this investigation.

Ammonia treatment: The AC was placed as a thin layer at the bottom of a quartz boat which was then inserted into the centre of a horizontal reactor. The reactor was heated to different temperatures (400-680 °C) at a heating rate of 5 °C min⁻¹ under a nitrogen flow of 9 L h⁻¹. Then ammonia (12 L h⁻¹) was introduced into the reactor for 2 h. The reactor was finally cooled to room temperature under a nitrogen flow. Additionally, the SC-AC-02 samples oxidized with air (SC-AC-02-300/0.5 air) and a mixture of nitric and sulfuric acids (SC-AC-02-NS) were subjected to amination at 450 and 700 °C. It has been expected that the pre-oxidation of carbon prior to amination can enhance N-doping due to the reaction of oxygen groups with ammonia [8]. The names of the obtained sample were the following: SC-AC-02-300air/700NH₃, SC-AC-02-NS/450NH₃ and SC-AC-02-NS/450NH₃.

Ammonia treatment under hydrothermal conditions: Hydrothermal treatment was performed in a steel-base home-made autoclave at 150 and 180 °C for 8 h. A 200 mL volume of AC (SC-AC-09) suspension in ammonia aqueous solution was placed into the autoclave and heated up to a desired

temperature with stirring. At 150 and 180 °C, the autogenic pressure was 3.6 and 8.7 bars, respectively. After the reaction, the autoclave was allowed to cool to room temperature, and the as-received N-AC samples were washed several times in deionized water and dried at 50 °C for 12 h. Samples obtained were labelled as SC-AC-09-HT150 and SC-AC-09-HT180.

Table 3.4 Characteristics of N-doped ACs obtained by different methods

Sample	Nitrogen content (wt. %)	Oxygen content (wt. %)	S_{BET} ($m^2 g^{-1}$)	V_T ($cm^3 g^{-1}$)	V_{DR} ($cm^3 g^{-1}$)	V_{DR}/V_T	L_0 (nm)
SC-AC-02	< 0.3	6.6	1402	0.62	0.49	0.79	0.91
SC-AC-02/450NH ₃	2.8	2.4	1136	0.50	0.41	0.82	1.02
SC-AC-02-300air/700NH ₃	3.3	2.3	969	0.43	0.34	0.79	0.91
SC-AC-02-NS/450NH ₃	5.5	5.6	768	0.34	0.29	0.85	1.03
SC-AC-02-NS/700NH ₃	4.6	2.9	780	0.34	0.28	0.83	0.95
SC-AC-09	<0.3	5.8	2306	1.01	0.80	0.79	1.14
SC-AC-09-400NH ₃	2.4	3.6	2205	0.94	0.75	0.80	1.05
SC-AC-09-450NH ₃	2.5	2.1	2237	0.98	0.77	0.79	1.06
SC-AC-09-500NH ₃	3.0	2.4	2171	0.95	0.74	0.78	1.06
SC-AC-09-680NH ₃	3.2	1.1	2127	0.92	0.74	0.80	1.20
SC-AC-09-HT150	5.2	6.0	2040	0.88	0.69	0.78	1.02
SC-AC-09-HT180	4.8	5.8	2070	0.90	0.70	0.77	1.03
SC-AC-09-350U	11.5	8.5	1500	0.64	0.52	0.81	1.11
SC-AC-09-450U	8.0	6.4	1780	0.76	0.63	0.82	1.05
SC-AC-09-550U	4.3	3.1	2080	0.90	0.72	0.80	1.02
SC-AC-09-650U	4.5	3.8	1960	0.85	0.69	0.81	1.01
SC-AC-10	<0.3	8.0	2630	1.15	0.90	0.79	1.25
SC-AC-10-450NH ₃	3.1	4.1	2560	1.12	0.87	0.78	1.20
SC-AC-11	<0.3	5.9	2830	1.26	0.92	0.73	1.33
SC-AC-11-450NH ₃	2.4	2.5	2770	1.27	0.91	0.72	1.30
P27-AC/800-3	<0.3	4.2	2020	0.91	0.70	0.77	1.06
P27-AC/800-3-500/2 NH ₃	2.6	2.1	1820	0.82	0.63	0.77	1.08

Urea treatment: The AC sample was impregnated with saturated urea aqueous solution of appropriate volume in order to obtain the mass ratio of AC to urea as 9:1. The mixture was stirred at room temperature for 5 h. After evaporation of water, the sample impregnated with urea was carbonized in nitrogen at a heating rate of 10 °C min⁻¹ to different temperatures in the range of 350-650 °C and maintained at a desired temperature for 1 h. The as-received sample was washed several times with boiling distilled water to remove excess decomposition products, filtered and dried at 110 °C to constant weight. The urea-treated samples were labelled as SC-AC-09-temperature of treatment U (urea), e.g. SC-AC-09-350U.

Figure 3.7 shows the nitrogen isotherms and the pore size distribution determined based on the adsorption data for ammonia-treated SC-AC-09 (a, b) and urea-treated SC-AC-09 (c, d). All the N₂ isotherms are of type I, indicating the microporous nature of N-ACs. Similarly, to the initial ACs (SC-AC-02, SC-AC-09, SC-AC-10, SC-AC-11, P27-AC), the N-ACs obtained are characterized by developed microporosity ($V_{DR}/V_T > 0.72$).

The characteristics of N-doped ACs were listed in Table 3.4, including the nitrogen and oxygen contents and the textural parameters evaluated from isotherms obtained by N₂ sorption at -196.1 °C.

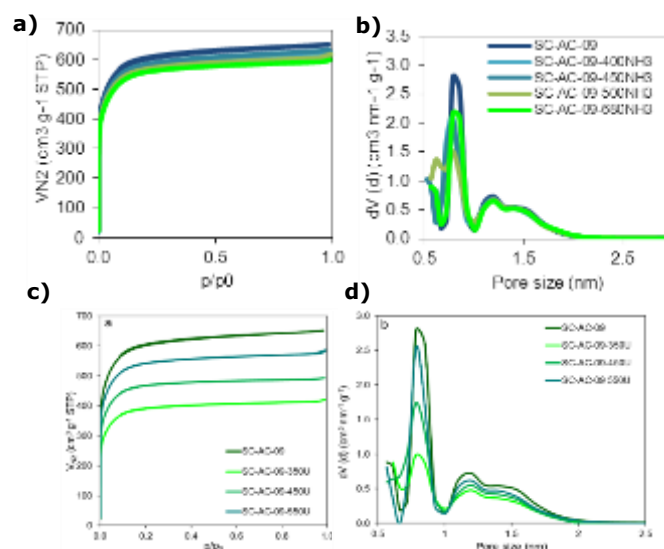


Figure 3.7 Adsorption-desorption isotherms of N_2 at $-196.1\text{ }^{\circ}\text{C}$ and the pore size distribution of (a, b) ammonia-treated SC-AC-09 and (c, d) urea-treated SC-AC-09.

All ammonia treatments are related to the loss of weight because of the reaction of the AC with ammonia at temperatures of $400\text{--}700\text{ }^{\circ}\text{C}$. The highest weight loss, over 32 %, is observed for the SC-AC-02 oxidized with a mixture of acids and subsequently subjected to reaction with ammonia. This finding indicated that the wet oxidation is unsuitable method for pre-treatment of AC prior to amination. Supposedly, the oxygen groups, which were formed on wet oxidation (17.9 wt. %), are decomposed or react with ammonia, leading to a high weight loss. A loss of weight of about 10 % only is obtained for the SC-AC-02 oxidized at $300\text{ }^{\circ}\text{C}$ with air and then treated with ammonia. However, in this case the pre-oxidation followed by amination leads to a drastic decrease in the BET surface area by 45 %, from 1402 to $768\text{ m}^2\text{ g}^{-1}$. Therefore, a direct amination of AC using ammonia was selected as an N-doping method in a further study. The treatment of SC-AC-02 with NH_3 at $450\text{ }^{\circ}\text{C}$ resulted in nitrogen doping level of 2.8 wt. %. The S_{BET} value decreased from 1402 to $1136\text{ m}^2\text{ g}^{-1}$.

In the next step, SC-AC-09 of higher specific surface area than SC-AC-02 (2306 vs. $1402\text{ m}^2\text{ g}^{-1}$) was subjected to amination at different temperatures, ranging from 400 to $680\text{ }^{\circ}\text{C}$, in order to optimize the temperature of ammonia treatment. The highest both the nitrogen content and the BET surface area were considered as criteria of the evaluation. More nitrogen was introduced into the carbon surface with increasing temperature of amination, reaching a maximum content of 3.2 wt. % for the SC-AC-09 modified at $680\text{ }^{\circ}\text{C}$. However, an increase in the nitrogen content was followed by a decrease in the BET surface area, up to $2171\text{ m}^2\text{ g}^{-1}$. The temperature of $450\text{ }^{\circ}\text{C}$ was found as optimal for the reaction of AC with gaseous ammonia. The same temperature was applied to SC-AC-10, obtaining a carbon with 3.1 wt. % nitrogen and a slightly reduced S_{BET} from 2630 to $2560\text{ m}^2\text{ g}^{-1}$.

For the N-ACs obtained, the contribution of micropores in the total pore volume is in the range of 0.72–0.83. The pore size distribution determined by the QSDFT method revealed that after amination at $680\text{ }^{\circ}\text{C}$, the SC-AC-09-680NH₃ exhibits wider microporosity compared with the N-ACs obtained at lower temperatures. This result indicates the active role of ammonia as a gasification agent at high temperatures. It is interesting to notice that an increase in the temperature of amination, from 400 to $680\text{ }^{\circ}\text{C}$, does not affect so much the BET surface area, which is between 2127 and $2237\text{ m}^2\text{ g}^{-1}$ for N-SC-AC-09 series.

Another approach to introduce nitrogen into the AC structure was based on the reaction of AC with urea. The effect of temperature treatment on the elemental composition and porous structure was determined. With temperature increasing from 350 to $650\text{ }^{\circ}\text{C}$, the nitrogen content in the N-AC decreases from 11.5 wt. %, reaching a minimum at $550\text{ }^{\circ}\text{C}$ (4.3 wt.%), and then slightly increases. An enhanced nitrogen content in the samples modified at 350 and $450\text{ }^{\circ}\text{C}$ suggests that these temperatures are not enough for complete decomposition of urea. The same trend is observed in the case of oxygen content. The changes in the porous texture confirm this finding. The largest drop in the BET surface area is observed at 350 and $450\text{ }^{\circ}\text{C}$ due to pore blocking by products of urea partial decomposition. The S_{BET} of the unmodified carbon was $2306\text{ m}^2\text{ g}^{-1}$. The BET surface area of the modified SC-AC-09 increases from 1500 at $350\text{ }^{\circ}\text{C}$ to $2080\text{ m}^2\text{ g}^{-1}$ at $550\text{ }^{\circ}\text{C}$, being slightly lower for SC-AC-09 treated with urea at $650\text{ }^{\circ}\text{C}$ ($1960\text{ m}^2\text{ g}^{-1}$). Compared with amination, the reaction with urea leads to higher reduction of the BET surface area. For all urea-treated ACs, the contribution of the micropore volume in the total pore volume is comparable, 0.80–0.82. It is interesting, that with increasing temperature, the average pore width L_0 of the modified AC

increases in case of treatment with ammonia but decreases when urea was used as an N-dopant. When we compare the average micropore width of ACs of highly developed surface area ACs, i.e. SC-AC-09, SC-AC-10 and SC-AC-11, it is clear that the incorporation of oxygen and nitrogen groups results in narrowing pores in their porous structure, which is supported by lower pore width of the initial ACs. There is a different impact of N-dopant on the pore size distribution of the N-ACs obtained at increasing temperature. In case of urea-treated SC-AC-09, the shape of PSD profile of N-ACs is nearly the same, indicating a proportional decrease in the volume of micropores in the whole size range. For ammonia-treated SC-AC-09, the impact on the narrow micropores is predominant.

The reaction of P29-AC/800-3 with ammonia at 500 °C for 2 h yields the carbon with a 2.6 wt. % of nitrogen and a S_{BET} of 1820 m² g⁻¹, which is approximately 10 % lower than that of the initial AC. A reduction of oxygen, from 4.2 to 2.0 wt. % occurred due to ammonia treatment.

In all cases, the modification of AC leading to the introduction of nitrogen on the carbon surface resulted in decreases in the total pore volume and the micro- and mesopore volumes and slight changes in the contribution of micropores in the total pore volume. The extent of the reduction of textural parameters was related to the N-doping method, process parameters and porosity development of the initial AC. Hydrothermal treatment with ammonia leads to a higher nitrogen content (4.8-5.2 wt. %) compared with amination (2.4-3.2 wt. %), but the reduction of the BET surface area takes place to a higher extent (11.5 vs. 7.8 %).

Work Package conclusions:

- A laboratory method for chemical activation was developed and applied.
- A representative number of experiments of chemical activation by microwave field were carried out.
- Microwave technologies determine changes in adsorption characteristics of the activated carbons highlighted by variation of different parameters as: type of microwave heating; quality of carbon precursors (AO pitch coke); temperature of carbon precursor making (450-480 °C); activation temperature (700 °C); duration of the activation/soak time (60-120 min) at maximum temperature.
- Green coke (of 450 °C) is suitable for chemical activation and obtaining surface area S_{BET} over 2200 m² g⁻¹. The reason is that the interaction of KOH is more effective in coke of 450 °C, less carbonized compared to that of 480 °C, which has an increased carbon structural organization and thus, is more resistant to attack by KOH.
- The temperature increases to obtain a carbon precursor (480 °C) causes a decrease in the adsorption capacity thereof expressed by S_{BET} which shows values by 2000 m² g⁻¹. The decrease is noted also in the case of variation of the ratio C:KOH used in chemical activation.
- Chemical activation by 700 °C produces typical changes for this type of material: extension of pores with weight loss increasing starting with the ultra-microporosity, which is gradually transformed in micropores and then in mesopores.
- The activation mode of KOH shows:
 - (i) the reactant acts after the pyrolysis of the precursor, at temperatures at 700 °C;
 - (ii) the development of porosity relates to the extent of impregnation by the KOH;
 - (iii) initially, narrow microporosity is formed followed by the wider microporosity at the expense of the narrow microporosity under 20 Å typical for molecular sieves;
 - (iv) high ratios of KOH to carbon result in increased expanding and flocculation of the carbon granules with a low density;
 - (v) structures within green cokes (450 °C) are less strongly bonded together compared with the carbonized coke of 480 °C (harder material);
 - (iv) during microwave heating and increasing temperature up to 14 °Cmin⁻¹, the intercalated compound becomes unstable and with rapid heating the alkali metal is explosively desorbed and by so doing, destroys the structures in which it was initially located.
- The optical microstructural studies on the activated carbon, intend to reveal the different appearance of textures in chemical activation. The original character of our research is emphasized by the attempt to correlate different type of carbon textural aspects with their higher or smaller susceptibility and/or selectivity, versus the activating agent. The photomicrographs of the activated carbons show characteristic images for the degassing evolution stages during the chemical activation progress. Depending on carbon type (green coke) they reveal the decreasing of porosity

up to a certain limit. After that, the progressive weight loss of carbon substance takes place which lead to the pores enlargement and the decreasing of the adsorption surface.

- The main effort in the modification of AC was put on elaborating the method for introduction of oxygen or nitrogen into the carbon structure with a minimal drop in the surface area of the pristine AC. Comparison of the wet oxidation method using different oxidants, dry and electrochemical oxidation revealed that the oxidative treatment of AC with air is the most effective approach, leading to increased oxygen content and a few percent drop in surface area only. For N-doping AC, heat treatment with ammonia at high temperature is recommended as a suitable method to obtain N-ACs with relatively high nitrogen content and preserved surface area of the pristine AC to a high extent. The hydrothermal treatment of AC with ammonia and modification with urea resulted in a significant decrease in the porosity development, although the N doping level was higher compared with thermal treatment with ammonia.

WP4. SYNTHESIS AND CHARACTERIZATION OF GRAPHENE (G) (INCAR-CSIC / IQNSA)

Task 4.1 Graphene from coal-liquid based graphites by the chemical route (INCAR-CSIC)

Several graphene materials were prepared by a modified Hummers method (Figure 4.1) starting from the different graphites synthesized by INCAR-CSIC (Task 1.4) [9]. Three of the graphites were obtained from "conventional green cokes" from IQNSA (SC-Gr-01, SC-Gr-05 and SC-Gr-07) and three other ones from green cokes derived from microwave-based precursors (SC-Gr-CTR-01, SC-Gr-CTR-02 and SC-Gr-CTR-03). Moreover, graphene materials were also obtained from a coal tar (CT) precursor (SC-Gr-CT-01) instead of the commonly used AO ones (conventional technology).

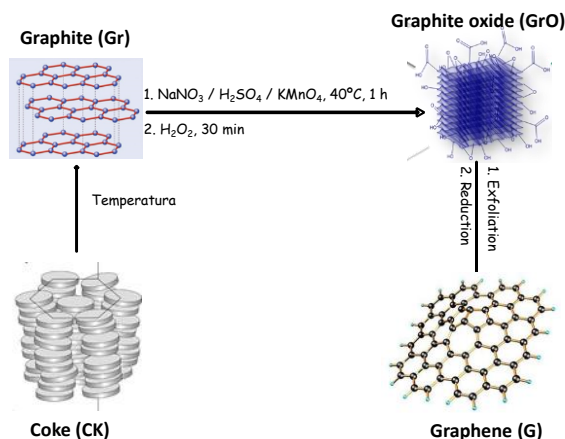


Figure 4.1 Scheme followed for the synthesis of graphene materials by the chemical route

In a first step the oxidation of such graphites consists on treating them with NaNO₃ and KMnO₄, in a ratio of 2:1:6 by weight, in presence of H₂SO₄ acting as a solvent. After 1 h at 40 °C and vigorous stirring, a solution of H₂O₂ (3 wt. % in water) was added to stop the reaction and to neutralize the excess of KMnO₄ used. Then the residual permanganate salts were eliminated by repetitive sedimentation steps by centrifugation (5 times with deionized water and 2 times with MilliQ water). After removing the solvent by evaporation in a rotavapor, a solid graphite oxide (GrO) was obtained.

In a subsequent step the as obtained graphite oxides were subjected to a thermal exfoliation/reduction process to be transformed into partially reduced graphene oxides (GOs). For this purpose, a stainless steel reactor designed by INCAR-CSIC was used at a T of 300 °C (this T was previously selected as that required for the blasting, as a consequence of the release of water and labile oxygen functional groups) [10].

Considering the characteristics required for an active electrode material in electrochemical energy storage devices (mainly in terms of specific surface area, chemical composition and electrical conductivity) the SC-TRGOX-300 samples were further thermally reduced (in a tubular furnace with a heating ramp of 5 °C min⁻¹ and under N₂ flow) for which purpose 700 and 1000 °C were selected as proper T. The graphene materials obtained were labelled as SC-TRGO1-700, SC-TRGO1-1000, SC-TRGO5-700, SC-TRGO5-1000, SC-TRGO7-700, SC-TRGO7-1000 when starting from AO derived graphites (conventional technology); SC-TRGO1-CTR-700, SC-TRGO1-CTR-1000, SC-TRGO2-CTR-700, SC-TRGO2-CTR-1000, SC-TRGO3-CTR-700, SC-TRGO-CTR-1000 when starting from the graphites derived from the microwave technology and SC-TRGO1-CT-QN-700, SC-TRGO1-CT-QN-1000 when starting from the coal tar derived graphite (also conventional technology).

All of them were preliminary characterized by SEM (Figures 4.2 and 4.3), elemental analysis and N₂ adsorption at -196.1 °C (Table 4.1)

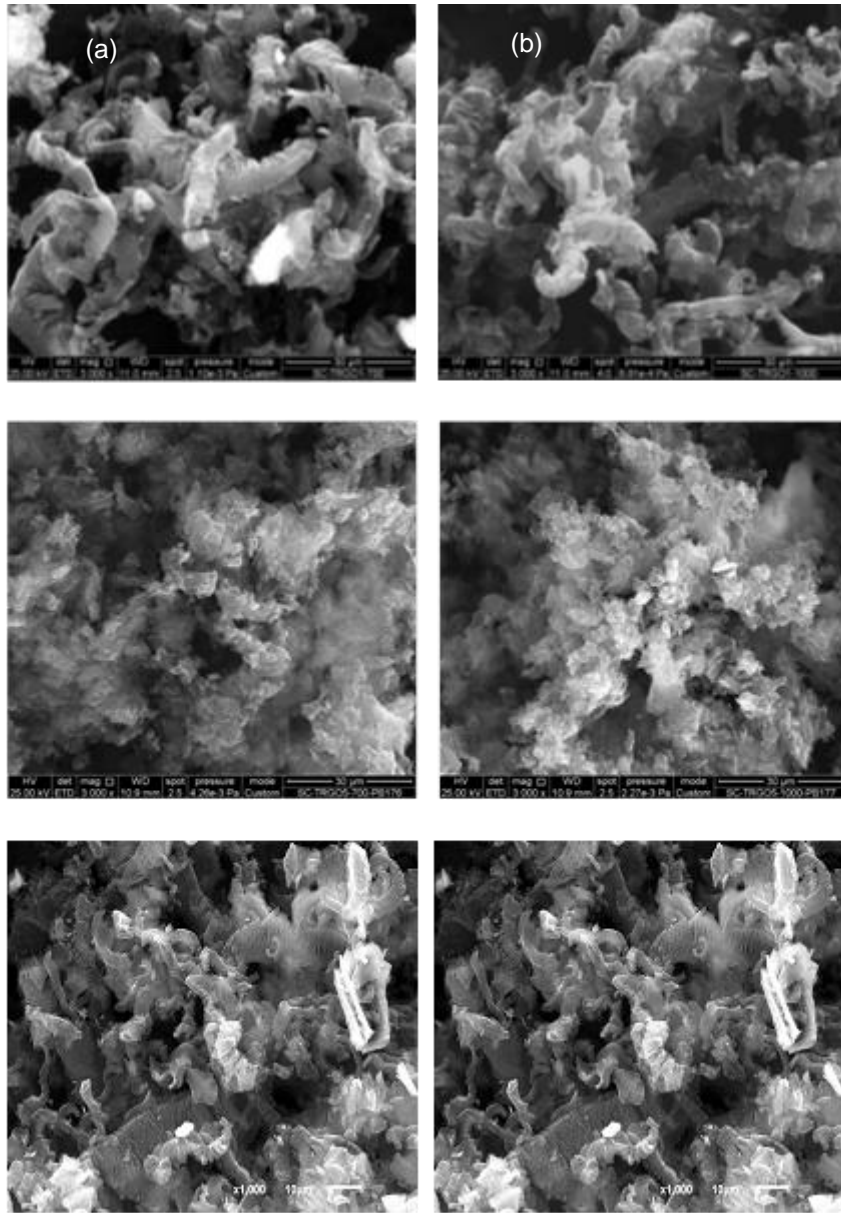


Figure 4.2 SEM micrographs of the (a) SC-TRGO1-700 (b) SC-TRGO1-1000 (c) SC-TRGO5-700 and (d) SC-TRGO5-1000 samples (e) SC-TRGO7-700 and (f) SC-TRGO7-1000 samples

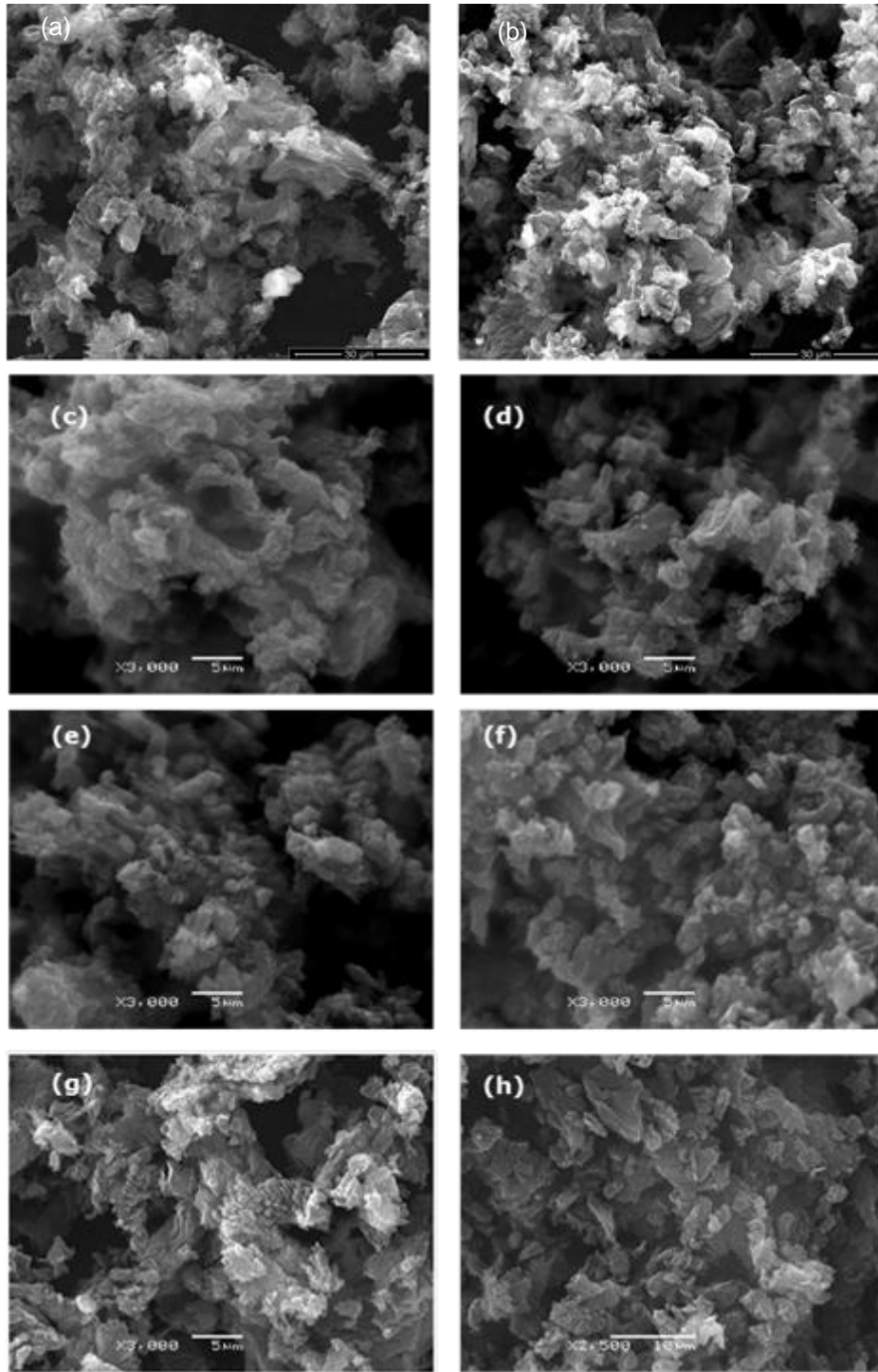


Figure 4.3 SEM micrographs of the (a) SC-TRGO1-CTR-700 (b) SC-TRGO1-CTR-1000 (c) SC-TRGO2-CTR-700 (d) SC-TRGO2-CTR-1000 (e) SC-TRGO3-CTR-700 (f) SC-TRGO3-CTR-1000 (g) SC-TRGO1-CT-QN-700 and (h) SC-TRGO1-CT-QN-1000 samples

Table 4.1 Characteristics of the main graphene materials obtained

Sample	Elemental analysis (wt. %)					S_{BET} (m^2g^{-1})
	C	H	N	S	O	
SC-TRGO1-700	90.6	0.5	0.2	0.0	8.6	490
SC-TRGO1-1000	98.1	0.3	0.3	0.0	1.3	477
SC-TRGO5-700	88.5	0.8	0.2	0.0	10.5	580
SC-TRGO5-1000	97.8	0.2	0.5	0.0	1.5	533
SC-TRGO7-700	91.6	0.8	0.0	0.0	7.6	454
SC-TRGO7-1000	98.4	0.4	0.1	0.0	1.1	477
SC-TRGO1-CTR-700	91.6	0.8	0.7	0.0	6.8	455
SC-TRGO1-CTR-1000	98.4	0.5	0.7	0.0	0.4	422
SC-TRGO2-CTR-700	91.9	0.6	0.2	0.0	7.3	524
SC-TRGO2-CTR-1000	98.0	0.8	0.4	0.0	0.8	492
SC-TRGO3-CTR-700	92.0	0.5	0.2	0.0	7.3	538
SC-TRGO3-CTR-1000	98.0	0.8	0.4	0.0	0.8	490
SC-TRGO1-CT-QN-700	95.6	1.4	0.3	0.0	2.7	411
SC-TRGO1-CT-QN-1000	97.5	0.6	0.8	0.0	1.0	396

According to SEM images shown in Figure 4.2 the materials obtained from SC-Gr-01 and SC-Gr-07 seemed to be not completely exfoliated which could be explained the characteristics of the cokes used as precursors in the synthesis of the subsequent graphites. In this context, different procedures were followed in order to obtain materials completely exfoliated. On one hand, more aggressive thermal exfoliation/reduction temperatures were applied to the corresponding graphite oxides (460 and 700 °C) without better results than the previously ones. On the other hand, an optimization of the Hummers method was proposed trying to achieve a better oxidation of the starting graphite. Thus, SC-Gr-01 was subjected to a second Hummers procedure but modifying the ratio of reactants (1:1:6 - Gr: $NaNO_3$: $KMnO_4$) and the time of reaction (from 1 to 3 h). The resultant graphite oxide was subsequently thermally treated at 300 °C in the reactor. As in the samples firstly obtained, the thermally reduced graphene oxide showed an accordion-like structure characteristic of non-completely exfoliated materials.

In order to evaluate the influence of the coke selected as raw material, another coke also supplied by IQNSA but not corresponding to the batches of the present project, was used (SC-CK-AO-QN-05). Thus, the corresponding graphite (SC-Gr-05) was subjected to the Hummers method and thermally exfoliated/reduced following the conventional treatment. The resultant samples (SC-TRGO5-700 and SC-TRGO5-1000) were completely exfoliated according to the corresponding SEM images, thus presenting higher specific surface areas (Table 4.1).

Even though not been properly exfoliated, also the graphene materials from SC-Gr-01 and SC-Gr-07 were considered for their subsequent electrochemical characterization.

Regarding the materials obtained from the microwave derived precursors and de coal tar-based graphite from conventional technology (Figure 4.3) they seemed to be completely exfoliated although some accordion-like structures can be still found in the series SC-TRGO1-CT and SC-

TRGO1-CTR. This represents a significant difference when comparing with those graphenes synthesized from AO derived precursors by conventional technology (previously reported) where worm-like structures were predominant.

When analysing the data summarized in Table 4.1 it should be emphasized the higher S_{BET} values and the lower oxygen contents of the CTR samples comparing with the CT ones. Moreover, these values have been also improved (mainly in the case of series SC-TRGO2-CTR and SC-TRGO3-CTR) with respect to the previously similar graphene materials obtained by the conventional technology (SC-TRGO1-700 and SC-TRGO1-1000). These promising results seemed to indicate that the microwave technology could be an alternative route to the synthesis of graphene materials comparable or even better to the conventional ones which was subsequently evaluated from the point of view of the electrochemical measurements (Task 6.2).

Task 4.2 Graphene from direct exfoliation of coal-liquid based graphites by using supercritical fluids (IQNSA)

This graphene synthesis path has a great potential for scalability, because it is a continuous process, apparently simple and does not generate waste.

It is a process of direct exfoliation of graphite by wet process in which a series of carriers or appropriate reaction media are used in which, when exposed to certain pressure and temperature conditions, give rise to the exfoliation of the graphite layers.

Two types of liquid and gaseous carriers can be used. The use of liquid carriers allows functionalization of graphene, either via specific ligands or nucleated nanoparticles on its own laminar structure, while the use of gaseous carriers makes the process cheaper and more scalable by requiring less extreme conditions. On the other hand, the use of liquid carriers allows the use of this method continuously, while for the use of gaseous carriers the design of a continuous method is a technological challenge to be carried out.

This productive method has used innocuous carriers (water, CO_2 , N_2 , etc. ...) that have eliminated the generation of waste from the graphene production process, giving rise to a green technology without environmental impact.

During the development of the project, this technology has been studied exhaustively to determine its potential as a scalable and sustainable graphene manufacturing method.

In parallel a similar procedure was carried out using cokes (instead of graphites) as starting materials.

For this task 4.2, two ways have been followed:

- Indirect wet exfoliation via graphite oxide with Water Peroxide in a water supercritical condition
- Direct wet mechanical exfoliation with an Ultra-Turrax equipment

Indirect wet exfoliation via graphene oxide

In this way oxidation of starting coke or graphite with hydrogen peroxide was carried out providing graphene oxides and their partial reduction products.

In this method a graphite or coke water suspension is brought to supercritical conditions of pressure and temperature (221 bars, 375 °C). At this point vapor and liquid conditions are so close that only one phase is formed (supercritical phase) with properties between liquids and gases.

Taking into account the special solubility of oxygen in this supercritical phase and to the changes in the density of the medium the different compounds of the mixture can be in close contact. In addition, because of the high temperature and the molecular density of the medium, the oxidative reaction takes place quickly and completely. To improve the oxidant capacity of the medium H_2O_2 (30-50 wt. %) was added. Considering the high energy of the medium a high concentration of oxygen radicals is formed, and due to the low surface tension of a supercritical fluid, those radicals could reach the interplanar surface of the starting material, oxidizing their corresponding layers.

To carry out the direct wet exfoliation of the different starting materials investigated IQNSA has acquired a special reactor ("autoclave") designed to withstand the high temperature and pressure conditions needed (Figure 4.4). The reactor consists in a 2 L stainless steel tank heated by an electric system (500 °C). The reactor also counts with a pressure control which allows working at 350 bar using different gases (N_2 , O_2 , etc.).

For this purpose, the autoclave was implemented in the laboratory to be able to react under supercritical water conditions in a continuous way was built. The potential reactivity of H_2O_2 with

coke or graphite together with the possible radical decomposition of H_2O_2 has forced the reactor to be implemented with a huge number of safety measures. The resultant reaction pilot plant consists of 4 blocks (Figures 4.4).

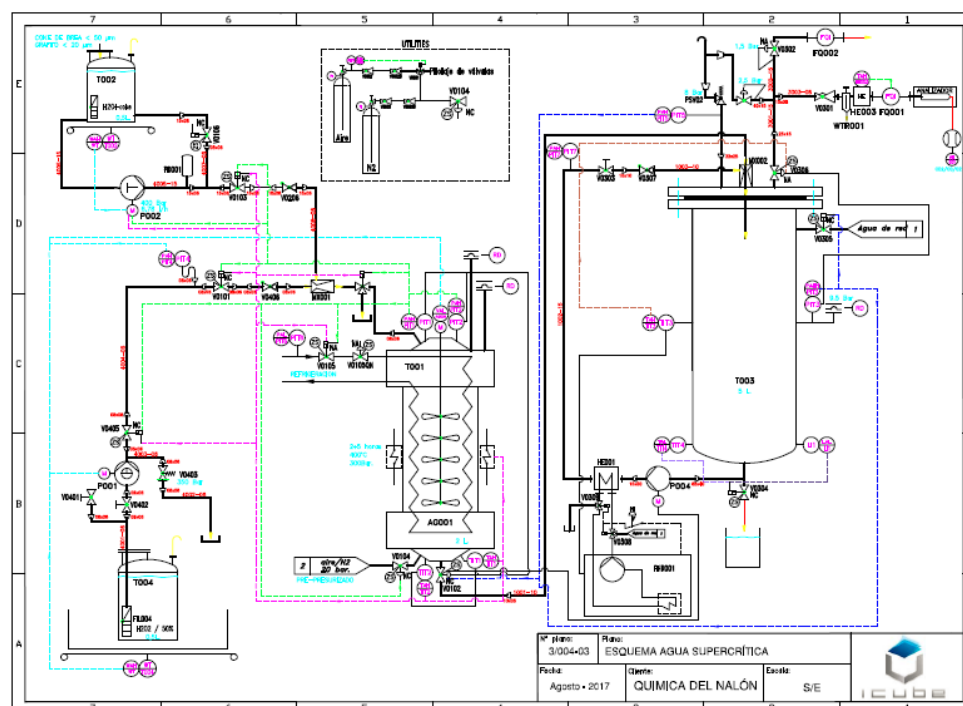


Figure 4.4 Global P&ID for the pilot equipped for direct exfoliation of coques/graphites by hydrogen peroxide under supercritical water conditions

Block 1. Reaction product feed block and additives

The addition block consists mainly of two pumps: a preparative pump for the hydrogen peroxide feeding and a dosing pump for the water suspension of the sample, capable to feed the mixture up to 400 bars.

To avoid that there is no injection of fluid in the circuit of the opposite pump, there are two check valves preventing the opposite direction of the fluid. Thus, both flows will enter the static mixer generating a mixture of these before entering the injection point. As a safety feature, connected to the static mixer inlet, there is a 3-way valve for linking the contents to waste or to process as desired.

The stretch of the preparative pump is dimensioned with the greatest safety restrictions to perform a greater control over the dosage of the compound that is decided to add to this line. The preparatory pump has the option to choose the operating flow rate, dosing the fluid with a more than considerable precision. In any case, it has been decided to place a balance on which the bottle rests, from which the absorption of fluid is carried out to have a greater control over the quantity dispensed. If this scale registers a greater weight decrease than expected, it will generate the automatic stop of the pump.

Likewise, in the drive section there are two pneumatically operated valves that will have a double operating command, on the one hand, a double signal of the internal temperature of the injection point to process, and on the other hand a double signal of the internal pressure of that same point.

Finally, highlight the operation mode of both pumps. These are capable of pumping fluid up to the pressure of 400 bar (as indicated at the beginning of this section), but they work by setting a flow rate and not a pressure. In this way, it is ensured that the flow delivered is the one defined in the preparation of both pumps. Each pump supplies this flow by overcoming the pressure losses that are in its path and at the point of supply, so that they will never operate above the set pressure to which the injection point can operate.

Block 2. Reaction gas analysis block

The connection point is in principle designed to be connected directly from the reactor. In any case, its usual location will be through the expansion / cooling tower that will be described in "Block 3".

The main line has pressure control valve upstream of 2 bars to ensure sufficient pressure and flow for the gas analysis (1 bar, 1 L min⁻¹). The rest of the flow (150 L min⁻¹ max) would pass through the vent line with a flow meter / totalizer.

In the case of an excessive flow of gases (> 150 L min⁻¹), which cannot be admitted by both lines, line 3002 would be pressurized by opening a valve to dislodge all gases.

In the feeding line of the analyser a pressure control valve is housed to maintain the correct functioning of the equipment that is downstream of this. In this way, the gas linked to this section will do so at a pressure of 1 bar. To condition the gas prior to its analysis, condensate filtering and elimination will be carried out using two equipments consisting of a particulate filter and a Peltier cooler for moisture condensation.

Once the gas is conditioned, we will have a mass flowmeter by thermal dispersion equipped with a control valve. Therefore, a flow rate of 0.5 L min⁻¹ indicated for the correct functioning of the analyser will be set and it will be the same one that will perform the opening and closing of the valve so that this flow remains constant. The analyser continuously measures CO, CO₂ and O₂; all critical components of the reaction.

Block 3. Expansion / cooling block

This block will work when a continuous operation or the performance of a controlled depressurization from the reactor is required.

Tank T003 will perform the function. It is a 6-liter tank with 10 bar design pressure and 4 bar working pressure.

T003 has a pressure regulating valve capable of relieving 100 % of the flow coming from the pressure regulating valve of the reactor (to Block 2), contemplating the different pressure levels.

T003 keeps refrigerated water through an exchanger cooled with thermal fluid cooled through the refrigerator. It can regulate temperatures in the range 0-200 °C, with 1.5 KW · h in cooling and 2 KW · h in heating.

After the expansion from the reactor to 4 bar pressure, the temperature is reduced to 144 °C, but with a % of the water in excessive vapor phase; 70-80 %. That is why additional cooling is required to control the desired evaporation percentage.

In accordance with the thermal requirements of the system, the temperature of the cooling water will be regulated, and consequently the temperature of the cooling group.

At some point, the refrigerator could function in heating mode if a point evaporation of water is required.

The cooling water, contained in the bottom of T003, is in continuous recirculation from the bottom to the head of the tank. The flow rate of cooling has to be a volumetric flow rate 1:1 with respect to the vapours of the reactor.

The vapours of the reactor and the cooling fluid are mixed at the top inlet, after which with a direct heat exchanger they pass through a static mixer to improve the efficiency and then expand towards the cooling tower.

Block 4. Auxiliary Systems

In this block the auxiliary systems are implemented so that the reactor works in the optimum safety conditions.

- Implementation of the relief system
 - The existing reactor has two rupture discs calibrated to two different safety ranges.

- This relief system initially went directly to a safe external point
- The reconditioning includes:
 - Installation of a "Boiler" tank for pre-expansion and reduction of the speed of relief
 - Connexion to the same evacuation line
- Safety valve of the expansion tower "Block 3"
- Cooling tower of the rupture disc "Block 3"
- Relief due to over pressurization of "Block 2".
- Installation of an additional point for future extensions
- Include check valves in the connections of all lines to the relief network
- Compressed gas system for actuating control valves
- Figure 4.5 shows the evolution of the temperature and pressure profiles derived from the reactivity found in the reaction when it is added hydrogen peroxide at different temperatures. The system is not very sensitive to exothermicity with respect to temperature, but it is drastically sensitive to pressure. A 2 L reactor pre-loaded with 200 mL coke / H₂O₂ (30-50 %) and fed with 3.3 mL min⁻¹ H₂O₂ (50 %) a theoretical exothermicity of $\Delta H_r = -42 \text{ kJ min}^{-1}$ is obtained. In Figure 4.5 all additions were 5 mL per dose.

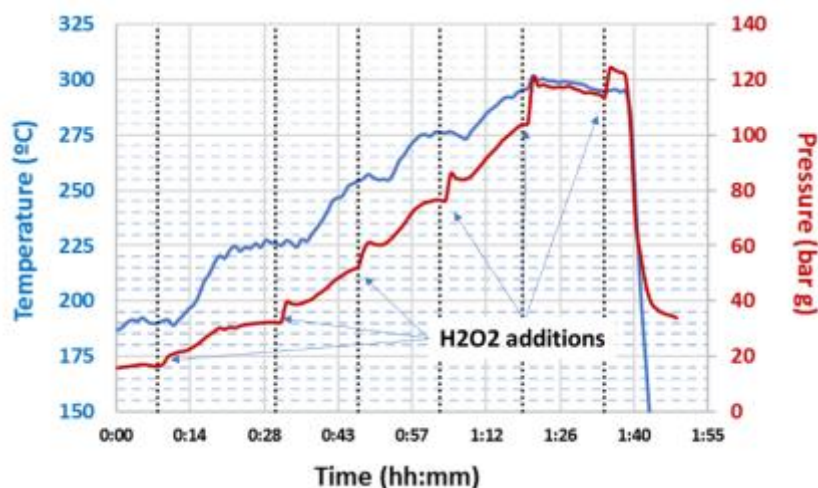


Figure 4.5 Exothermicity and overpressure found with the addition of hydrogen peroxide to the graphite suspension (10 %) at different temperature levels

Semi-continuous tests were conducted in May 2017 while continuous tests were conducted in October 2017-February 2018.

In the reaction, two types of raw materials were used: graphite and pitch coke. The most relevant results can be described as follows:

- It has been possible to establish a safe process of continuous reaction of coke / graphite with hydrogen peroxide.
- Although it is a laboratory equipment, the process allows 5 kg / day of coke / graphite to be processed (50 mL min⁻¹ of water / coke-graphite / H₂O₂ suspension being continuously fed)

- It has not been possible to obtain single-sheet graphene materials, as the reaction has not been still optimized. In any case, it allows exfoliating the graphene precursor properly for massive applications in composite materials with plastics, ceramics, etc.
- It allows producing stable aqueous suspensions of graphene materials as a preliminary step to obtain suitable dispersions for the manufacture of composite materials.
- The degree of disorder has increased, being able to be observed by an increase in the iodine index from 68 to 41 mg g⁻¹ for graphite and from 147 to 125 mg g⁻¹ for pitch coke.
- Derived from surface functionalization and etching to which the material has been subjected, the activation energy against oxygen has decreased from 40 to 27 kcal mol⁻¹.
- On the other hand, although the final granulometry of the product is equivalent (from the point of view of a laser diffraction device) -plot blue versus red-, a new fraction has been obtained (green plot), which represents 5 % of performance against the raw material used, with a substantially lower particle size (Figure 4.6).

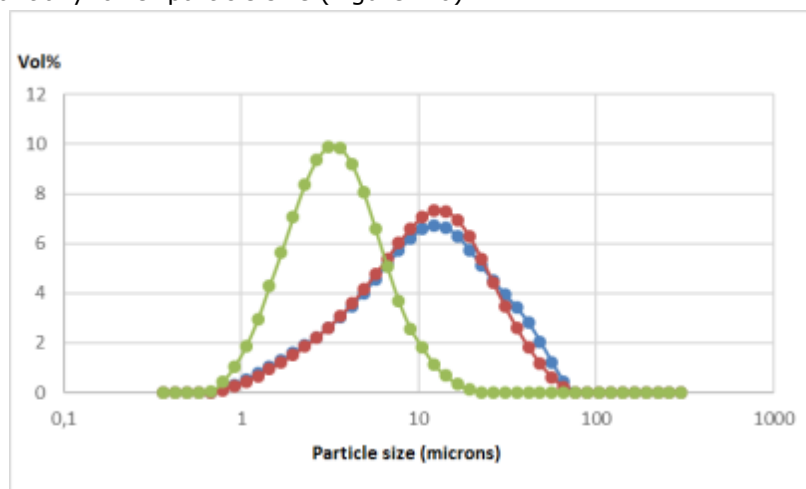


Figure 4.6 Particle size distributions because of hydrogen peroxide reaction with a coke. Blue line: Original product. Red line: global product after treatment. Green line: product obtained after filtration of the reaction product in a ceramic filter with 2 μm in size (initial coke has not any fraction passing the filter)

Operating method to work in continuous

Before starting any trial and for safety reasons it is necessary to have completed the Check-List that pre-set the equipment ready in a safe mode in a univocal way. Said document must be accepted and signed by the operators of the experiment and the Project Leader. A record in paper and electronic copy will be kept. These tests should NEVER be left unattended and require at least one supervising operator and another support person.

As safety precautions, before carrying out any continuous test, different reactivity study stages must be carried out for each sample and batch that is intended to be included in the process since small differences in metallic impurities or structural order can drastically alter the reactivity of the material versus hydrogen peroxide.

Direct wet mechanical exfoliation with Ultra-Turrax equipment

The procedure consists on the direct exfoliation of the starting material (graphite or coke) assisted by surfactants. These additives have been used for mechanical purposes, thus avoiding the use of oxidizing reagents.

In this way, what is called deep eutectic fluids are used, using a mixture of polyethylene glycol and choline chloride.

An aqueous suspension of graphite or coke / eutectic is subjected to a mechanical exfoliation process using Ultra-Turrax equipment (Figure 4.7), with the following operating principle:

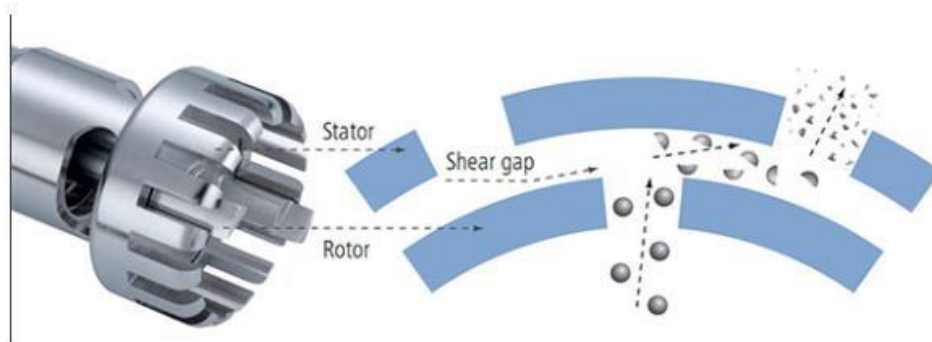


Figure 4.7 Operating principle of the mechanical exfoliation process

The stator remains motionless and the rotor rotates at about 10,000 rpm, allowing a grinding by exfoliation.

Once the material has been exfoliated, the subsequent agglomeration is inhibited since the surface tension of the eutectic exceeds the energy of the Van der Waals interaction of the graphite layers.

This allows obtaining stable suspensions of exfoliated graphite/graphene material to shorten the granulometric dispersion of the material; the sample is subjected to a centrifugation process at 2700 rpm-1 hour, obtaining the part in suspension as graphene material.

This part in suspension is filtered and washed with ethanol, achieving inks of alcoholic base, being able to recycle the eutectic.

In this way, a 16 wt. % yield of soluble graphite has been achieved, perfectly stable over time.

The precipitated obtained in the centrifugation process can be reprocessed back to the initial phase, increasing the final yield.

After setting up the process two samples were selected for further chemical characterization, one using coke as raw material and the other using graphite.

Both samples were previously filtered through a paper filter, analysing the liquid and solid fractions separately.

The liquid fraction was observed under the exposure of ultraviolet light observing a clear fluorescence as shown by the figure 4.8. This fluorescence has been demonstrated that is stable in the time at least in a 6 months' period.

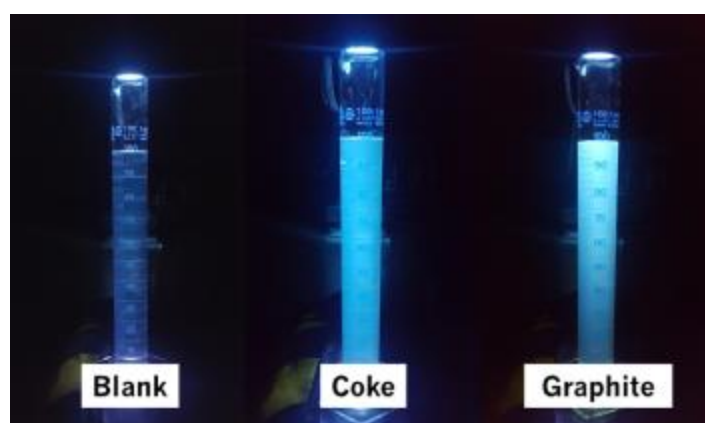


Figure 4.8 Aspect of the samples observed under ultraviolet exposure

This characteristic is typical of what is called Graphene Quantum Dots; an emerging material in the market right now.

Both samples gave rise to Q-Dots. However, the characteristics of each Q-Dots from each parent materials are different.

The Q-Dots from coke (Figure 4.9) are relatively homogeneous all along the sample. Most of the Q-Dots exhibit a height in the range of 2-5 nm, and a lateral size of 10-20 nm.

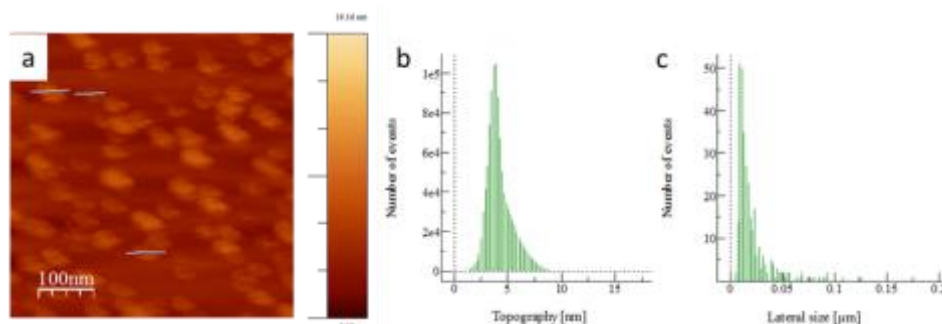


Figure 4.9 AFM images (a), topographic distributions (b) and lateral size (c) of Q-dots using coke

The Q-dots from graphite (Figure 4.10) are more heterogeneous along the sample. They exhibit a homogeneous height distribution but the lateral size is more heterogeneous, with a moderate number of Q-Dots of lateral size of 100 nm and above. That demonstrate that graphite is less reactive need a further process optimisation.

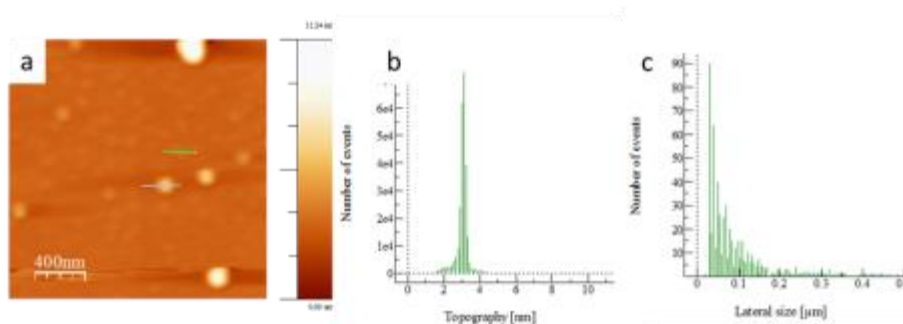


Figure 4.10 AFM images (a), topographic distributions (b) and lateral size (c) of Qdots using graphite

Coke solution emits more than the graphite one whether it is excited with a wavelength of 395 or 280 nm. When this last wavelength is excited, the emission band is centred at 375 nm, that is, they emit close to blue, whereas when they are excited at 395 nm, the emission band is centred at 500 nm (emits green).

For the graphite sample, a lower fluorescence is observed when it is excited at 395 or 280 nm centred at 375 nm, which suggests that it predominantly emits in blue.

The solid samples are composed by mixtures of exfoliated and non-exfoliated material. This is of importance in the case of the sample from graphite. Samples were re-filtered to facilitate characterization analysing the liquid phase. Again, it demonstrates that the process is not yet optimised.

The filtered solutions were evaluated by AFM (Figure 4.11).

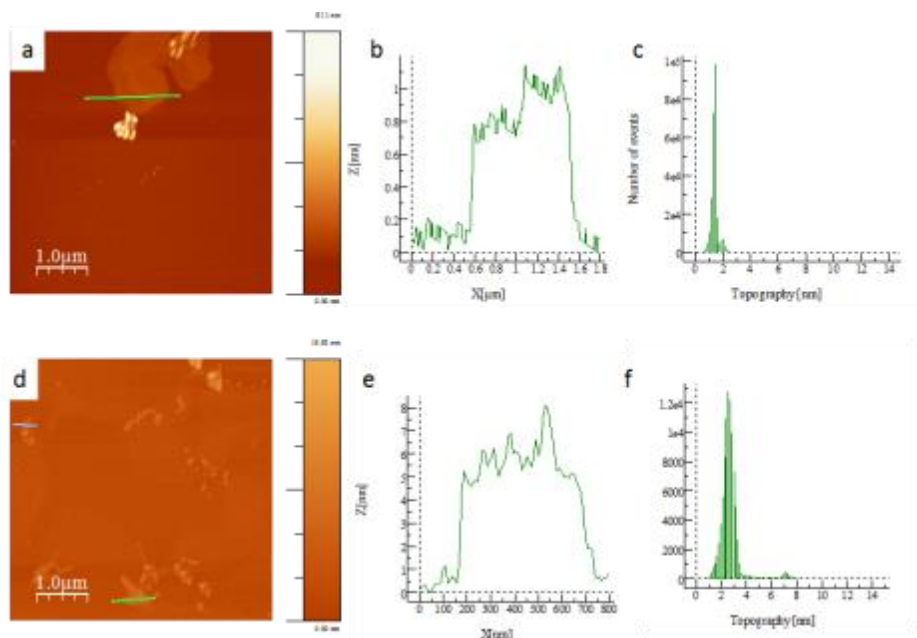


Figure 4.11 AFM Images (a, d), profiles (b, e) and topography (c, f) of the filtered superior fraction from coke (a, b, c) and graphite (d, e, f).

Results indicate that the graphene materials from coke (Figure 4.11, a, b and c) are larger (lateral size of 800 nm - 1 μm) and with an average height of 1.5 nm in the range of few layer graphene (Figure 4.10, a and b). In contrast, graphene materials from graphite, although exhibiting height in the range of few layer graphene materials (2-3 nm), are much smaller and heterogeneous in lateral size. Much of these graphite-based samples were composed by material of high height. This is also visualized in the analysis of the samples by STEM, in which it is possible to see in the graphite-based sample, large graphene layers coexisting with less exfoliated fractions (Figure 4.12, a). In contrast, the samples from coke are much smaller, in the range of those observed by AFM (Figure 4.12, b).

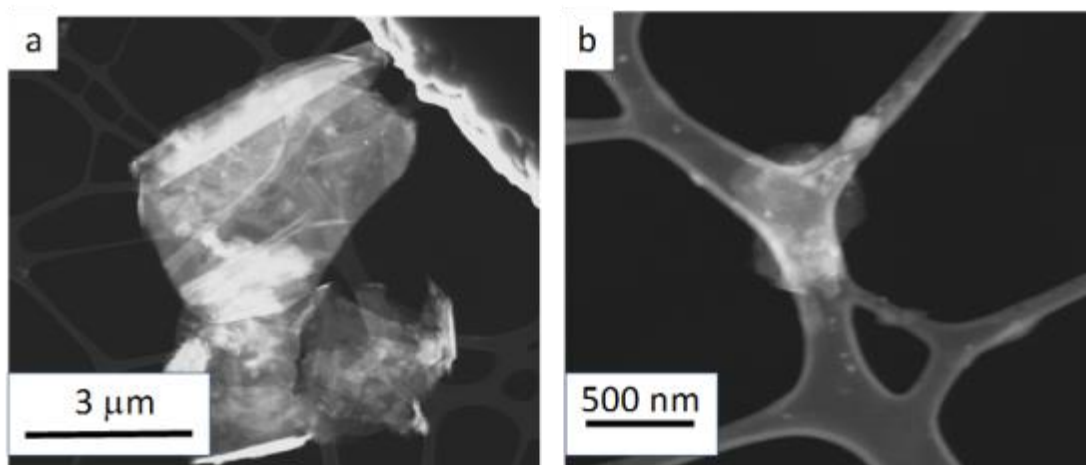


Figure 4.12 STEM images of graphene materials from graphite (a) and coke (b)

Work Package conclusions:

To obtain graphene materials INCAR-CSIC has followed a modified Hummers method starting from different graphites which were synthesized from coal-liquid based precursors derived from both conventional and microwave technologies. After the chemical oxidation of these graphites and the subsequent thermal/exfoliation procedure of the graphite oxide obtained as intermediate, the graphene materials synthesized from the conventional precursors seemed to be not completely exfoliated, according to the SEM characterization (showing an unexpected worm-like structure). On the other hand, the graphene materials from both coal tar and microwave derived precursors presented a better exfoliation, thus representing materials with comparable or even better characteristics than the previous ones (mainly in terms of morphology, specific surface area and

chemical composition), overall in those materials from microwave heating. These results represent a significant step in the development of alternative routes to synthesize graphene materials, mainly considering the lower time and energy consumptions of the novel route based of microwave heating.

Additionally, IQNSA has put into operation two alternative methods to the Hummers one, based on direct graphite exfoliation for the manufacture of graphene. Both procedures can be considered (i) sustainable, as they do not generate toxic wastes (ii) scalable, because they operate continuously and close to a capacity which could be appropriately scaled at the industrial level for the current market volume of these materials and (iii) economic, after having evaluated the energy, reagents and personnel costs required.

The way of obtaining graphene by the oxidation route with hydrogen peroxide under supercritical water conditions also offers the possibility of obtaining graphene oxide (a product also useful for different applications) with the peculiarity of being able to be thermally reduced by hydrothermal reduction in situ within the reaction / expansion stage simply by coupling an intermediate reservoir between the reactor and the expansion tower. The process also offers the possibility to obtain exfoliated materials directly from coke.

It has been also demonstrated that the process requires additional optimization as they produce heterogeneous samples, especially when graphite is used as raw material which could be explained considering its lower reactivity. Although these methods do not currently offer the quality of graphene materials offered by the Hummers method, they can be used in various applications that currently have a higher relative consumption.

Regarding the materials that have been obtained through oxidative exfoliation in supercritical water regime, the most important ones are the Graphene Quantum Dots. It is important to remark that, when compared to those currently offered in the market, those produced under the present project maintain their fluorescence over time. In any case, they require optimization in order to enhance their intensity.

Following the same operative procedure, standard graphite gives higher dispersion and heterogeneity. The process has also been carried out with coal tar pitch coke (without graphitization) thus showing the best results.

WP5. PREPARATION OF COMPOSITES ACTIVATED CARBON/GRAPHENE (AC/G) (INCAR-CSIC / UPB / CTRom)

Task 5.1 Synthesis of composite materials activated carbon/graphene (INCAR-CSIC / UPB / CTRom)

The aim of this task has been the synthesis of composites AC/G with the required characteristics (mainly in terms of S_{BET} and electrical conductivity) to be used as electrodes in the electrochemical devices investigated (symmetric supercapacitors and hybrid systems) [11]. With this purpose different routes were proposed, starting from ACs and different graphene materials as single precursors.

The first strategy followed, and mainly with comparative purposes, was the combination (by physical mixture) of different activated carbons and graphene materials (these last ones as conductive additives). Bearing in mind the characteristics required for suitable electrodes, two activated carbons (SC-AC-09 and SC-AC-10) and two graphene materials (SC-TRGO1-1000, as non-completely exfoliated material and SC-TRGO5-1000, as well exfoliated material) were selected. The two ACs mainly showed appropriate specific surface areas and textural properties. About the graphene materials it was necessary to achieve a compromise between their specific surface areas and electrical conductivities (related to the oxygen content) and, thus, those samples treated at 1000 °C were used. The mixture of both materials, with a 10 wt. % of the corresponding TRGO, was made by means of an Agatha mortar and later electrochemically characterized (see WP6).

Another route followed was the direct synthesis of an AC/G composite starting from an AC (SC-AC-11, as the first one obtained from a microwave derived carbon precursor exhibiting the highest specific area among the ACs) and a G precursor (a graphene oxide water suspension, SC-GO-05). After having optimized the ratio AC/GO = 2, the corresponding amount of the activated carbon was homogeneously dispersed into a certain volume of the graphene oxide water suspension (by sonication). The resulting stable suspension was treated following two different procedures:

- Solvent removal (evaporation in a rotavapor) and subsequent thermal treatment (up to 700 °C, tubular oven, N₂ flow) of the resultant solid. The composite thus obtained was labelled as [SC-AC-11/GO-05]-TR700. Also [SC-AC-10/GO-05-TR700], starting from an AC derived from conventional precursors, has been included with comparative purposes
- Hydrothermal treatment: the suspension was introduced in a Teflon reactor and thermally treated in a conventional furnace (180 °C, 19 h). After that, the resultant water was discarded and the solid was dried under vacuum prior to be used. The composite thus obtained was labelled as [SC-AC-11/GO-05]-HT180

Task 5.2 Preliminary characterization of the composite materials (INCAR-CSIC / UPB)

A preliminary characterization of the different composite materials was carried out by means of SEM (Figure 5.1). Furthermore, their textural and chemical properties have been summarized in Table 5.1. The advanced characterization of these materials was carried out inside WP7.

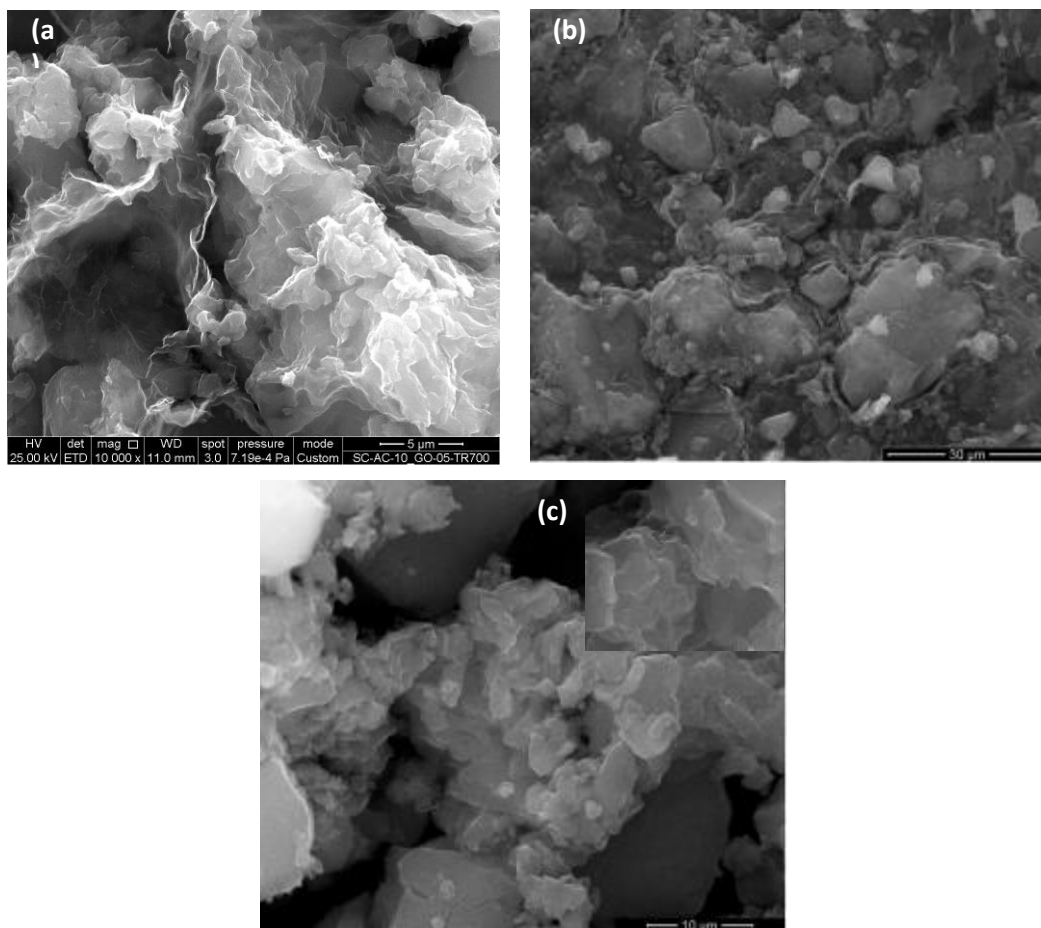


Figure 5.1 SEM micrographs of the composites (a) [SC-AC-10/GO-05]-TR700, (b) [SC-AC-11/GO-05]-TR700 and (c) [SC-AC-11/GO-05]-HT180

According to the SEM images, the graphene layers were homogeneously distributed through the whole material, wrapping the AC particles (mainly in the composite material from hydrothermal treatment), thus probing an intimate contact between the two single materials used as starting materials.

Table 5.1 Characteristics of the more representative composite materials produced

Sample	Elemental analysis (wt. %)					S_{BET} ($m^2 g^{-1}$)
	C	H	N	S	O	
[SC-AC-10/GO-05]-TR700	97.3	0.5	0.0	0.0	2.2	1800
[SC-AC-11/GO-05]-TR700	96.0	1.4	0.4	0.0	2.2	1934
[SC-AC-11/GO-05]-HT180	91.7	1.4	0.3	0.0	6.6	1615

As expected after the observation of the SEM images, in all the three materials the specific surface area decreased from that corresponding to the starting AC, mainly in the case of [SC-AC-11/GO-05]-HT180 thus representing an additional probe of the intimate contact between the two materials forming the composite, especially in that resulting from the hydrothermal treatment. In addition, this composite also exhibited a higher oxygen content, probably due to the residual functionalities in the partially reduced graphene oxide, than the measured on the other two AC/Gs (6.6 vs 2.2 wt. %). [SC-AC-11/GO-05]-TR700, with lower oxygen content and higher S_{BET} could show better electrochemical activity as electrode in SCs and hybrid systems. The three composite materials were electrochemically characterized in Task 6.2.

Work Package conclusions:

To obtain materials with enhanced electrochemical properties, composite materials have been synthesized, starting from ACs and graphene materials as single components, by following different strategies:

- (i) Simple physical mixture of AC and graphene material
- (ii) Direct synthesis of AC/G starting from an AC and graphene oxide (GO) as graphene precursor.

In this last case, after having optimized the amount of AC and the volume of GO water suspension the resulting suspension was treated in two ways:

- Solvent removal and thermal treatment of the solid
- Hydrothermal treatment of the suspension

In both cases, the obtained materials showed interesting properties. Even though their specific surface areas considerably decreased from that corresponding to the starting AC selected, a interesting morphology was observed with the graphene layers interconnecting the AC particles which could contribute to a better electrochemical performance of the thus obtained materials (mainly in the case of those from the hydrothermal treatment)

WP6. ENERGY STORAGE SYSTEMS: SUPERCAPACITORS (SCs) AND HYBRID SYSTEMS (TUWRO / INCAR-CSIC)

Task 6.1 Testing of active electrode materials in supercapacitors operating in aqueous electrolyte (TUWRO)

The aim of this part of research was an evaluation of benefit of AC modification for energy storage systems. The specific capacity of electrode material is the most important parameter for high performance supercapacitors. A significant increase of capacity was expected as an effect of extra faradaic reactions between the AC surface (pseudocapacity) and electrolyte. The influence of surface chemistry modification on the increase of over-potential of electrolyte decomposition and charge propagation at a high current load were analyzed. These factors allowed calculating and validating optimal configuration of electrodes in real asymmetric device. Asymmetrization of mass, specific surface area and surface chemistry of electrodes should allow balancing the different charge density vs. anions and cations and allow increasing the maximal operating voltage of capacitor.

The basic electrochemical behavior of the modified ACs was tested in a three-electrode Swagelok type cell system in 6 M KOH and 0.5 M Na₂SO₄ solution. The cell was built with gold current collectors. Hg/HgO (KOH) or Hg/Hg₂SO₄ (Na₂SO₄) was a reference electrode. The normalized, high porous activated carbon (MPK) was used as a counter electrode. The cyclic voltammetry (CV) at a scan rate of 2-100 mV s⁻¹ and galvanostatic charge-discharge (GCD) at a current density of 0.2-80 A g⁻¹ were performed using a Biologic VSP potentiostat-galvanostat.

A three-electrode Swagelok cell was also applied for testing of asymmetric capacitor. ACs of positive and negative electrodes and their mass ratio were selected based on the earlier estimated capacity behavior. The presence of a reference electrode allowed observing the work potential window of each electrode and, on this basis, to estimate the maximal charge voltage of the device.

The final cycling stability of asymmetric capacitor was carried out in the completely sealed 2-electrode Swagelok cell at several rated voltages.

The pristine ACs delivered by INCAR (SC-AC-SC-02, SC-AC-SC-09, SC-AC-SC-10, SC-AC-SC-11) and prepared by TUWRO (P-27-AC/800-3) were the subject of this study. The ACs modified by different oxidation methods, including electrochemical oxidation, wet and dry oxidative treatments (Task 3.3), and nitrogen-doping methods, using ammonia and urea as N-dopants (Task 3.4), were characterize in terms of their electrochemical behavior as an active material for supercapacitors.

Table 6.1 shows the gravimetric and specific surface capacitance values, the BET surface area and the oxygen content for the pristine and oxidized ACs.

Despite significant differences in the BET surface area of the pristine ACs (1400-2800 m² g⁻¹) the gravimetric capacitance is maintained at a similar level of 310-330 F g⁻¹. This finding can be explained by higher contribution of pseudocapacitance in the total electrochemical capacitance. Small differences in the specific capacitance values between ACs may also confirm that too much developed microporosity is useless for the capacitor performance. The total oxygen content in the pristine ACs is in a narrow range of 5.9-8.0 wt. %, but surface loading and electrochemical activity of oxygen is strongly different. Therefore, the specific capacity varies in the wide range from 11.7 μF cm⁻² (the most porous SC-AC-11) up to 22.1 μF cm⁻² (the least porous SC-AC-02).

Electrochemically oxidized ACs

The mild (EOX1) and moderate (EOX2) oxidation of SC-AC-09 allowed to introduce a noticeable amount of oxygen to the carbon structure (Table 3.3). As a result, pseudocapacitance is expected to contribute to the total gravimetric capacitance due to the presence of oxygen groups involved in redox reactions. However, a surface capacitance (C_s) is only slightly increased (Table 6.1). The work with electrochemical oxidation of AC was not continued because of insufficient effect.

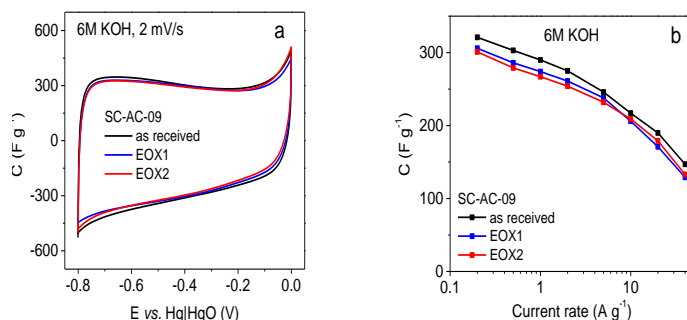


Figure 6.1 Electrochemical behavior of the pristine and electrochemically oxidized SC-AC-09 activated carbons

Air oxidized ACs

The air treatment leads to a decrease in the BET surface area by 2-10 %. However, it allows introducing oxygen functionalities to the carbon structure, which is beneficial due to pseudocapacitance effect. Therefore, the gravimetric capacitance of mild oxidized ACs is nearly maintained or is only slightly reduced (Table 6.1). As a result, the specific surface capacitance is then increased. However, a stronger air treatment is not beneficial, resulting in significant capacity decay due to a larger reduction of S_{BET} . The most of air-treated ACs show better performance at higher current rates compared with the non-oxidized ones. An example is given in Figure 6.2.

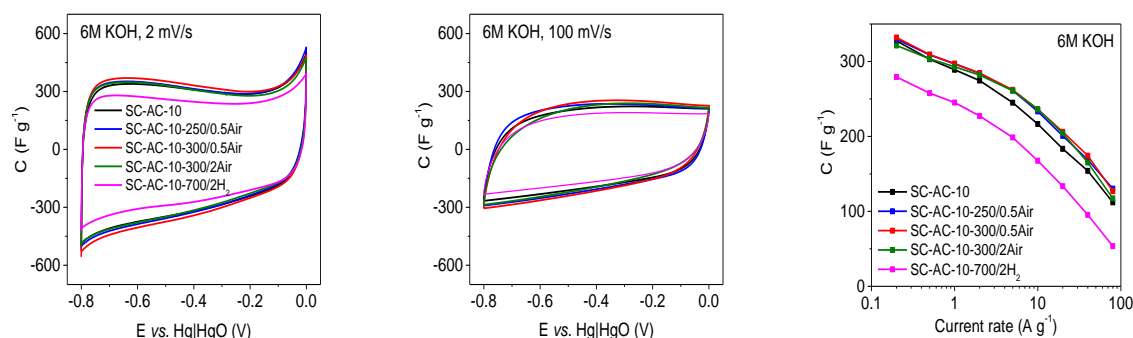


Figure 6.2 Electrochemical behavior of the pristine and air-oxidized SC-AC-10 activated carbons

Table 6.1 Gravimetric capacitance, specific surface area, oxygen content and specific surface capacitance of the pristine activated carbons, electrochemically and air-oxidized activated carbons.

Sample	C at 0.2 A g^{-1} (F g^{-1})	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	O (wt.%)	C_s ($\mu\text{F cm}^{-2}$)
SC-AC-02	310	1402	6.6	22.1
SC-AC-02-300/0.5 air	303	1261	7.3	24.0
SC-AC-09	322	2306	5.9	14.0
SC-AC-09-EOX1	306	2100	8.4	14.6
SC-AC-09-EOX2	301	2090	10.1	14.4
SC-AC-09-250/0.5 air	307	2296	6.4	13.4
SC-AC-09-300/0.5 air	303	2258	7.0	13.4
SC-AC-09-400/0.5 air	293	2024	10.0	14.5
SC-AC-10	328	2630	8.0	12.5
SC-AC-10-250/2 air	330	2520	8.7	13.1
SC-AC-10-300/0.5 air	332	2530	7.8	13.1
SC-AC-10-300/2 air	321	2480	9.4	13.0
SC-AC-10-700 H_2	279	2520	2.0	11.1
SC-AC-11	331	2830	5.9	11.7
SC-AC-11-300/0.5 air	334	2780	6.5	12.1
SC-AC-11-300/2 air	324	2662	7.8	12.2
SC-AC-11-350/0.5 air	322	2710	7.7	11.9
P27-AC/800-3	299	2020	4.2	14.8
P27-AC/800-3-300/2 air	277	1790	7.1	15.5

In order to emphasize the role of oxygen functionalities in the development of capacitance, SC-AC-10-700 was subjected to hydrogen treatment at 700 °C (SC-AC-10-700 H₂), resulting in a large decrease of oxygen content from 8.0 to 2.0 wt.%. The BET surface area decreased by only 4 %, but the specific capacitance was reduced to a much higher extent, by almost 15 %. No improvement of the rate capability was observed (Figure 6.2 c). The above results prove an important role of oxygen functionalities in the charge/discharge process.

Wet oxidized ACs

The oxidants used in this process, i.e. a mixture of nitric and sulfuric acids and ammonium persulfate, appeared to be very reactive towards ACs. As follows from the literature, these oxidants promote the formation of carbonyl and hydroxylic groups in contrast to nitric acid only. The applied treatments allow introducing to the carbon structure up to 30 wt. % of oxygen. However, the wet oxidation causes a significant reduction of the BET surface area of materials, resulting in a high decrease in the specific capacity of all modified ACs in comparison to the parent ones (Table 6.2). Moreover, when the oxygen content was higher than 18 wt. %, electrode materials show much worse performance at higher current loads due to higher inter-particle resistance (Figure 6.3).

Table 6.2 Gravimetric capacitance, specific surface area, oxygen content and specific surface capacitance of the pristine and wet oxidized activated carbons

Sample	C at 0.2 A g ⁻¹ (F g ⁻¹)	S _{BET} (m ² g ⁻¹)	O (wt. %)	C _s (μF cm ⁻²)
SC-AC-02	310	1402	6.6	22.1
SC-AC-02-NS	287	919	17.9	31.2
SC-AC-09	322	2306	5.9	14.1
SC-AC-09-NS	291	1999	13.5	21.6
SC-AC-09/1 AP	289	1960	21.1	14.8
SC-AC-09/24 AP	253	1560	29.7	16.2
SC-AC-09/1 AP 1:1	299	1950	17.8	15.3

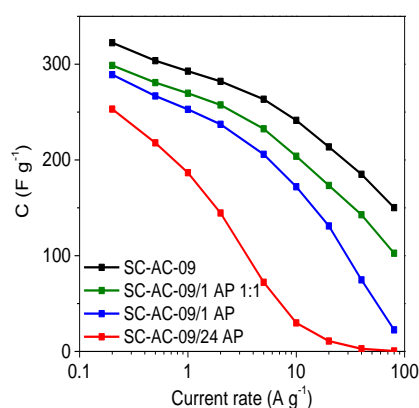


Figure 6.3 Electrochemical behavior of the pristine and ammonium persulfate-oxidized SC-AC-10 activated carbons.

Nitrogen containing ACs (N-ACs)

The gravimetric capacitance, the BET surface area, the specific surface capacitance, the contents of oxygen and nitrogen of N-ACs were presented in Table 6.3.

Up to 3.1 wt. % of nitrogen was introduced to the carbon surface by heat treatment of AC with gaseous ammonia (Table 3.4). Unfortunately, the BET surface area is reduced, and a part of oxygen functionalities is eliminated at the same time. As a result, an overall pseudocapacitance effect is not enhanced. The effect is pronounced at higher temperature treatment. Finally, the gravimetric capacitance of N-ACs at a low current rate is more or slightly lower than that of the pristine materials. A significantly better performance of the ammonia treated AC is observed at a higher current regime (Figure 6.4).

Table 6.3 Gravimetric capacitance, specific surface area, heteroatoms content and specific surface capacitance of the pristine and N-activated carbons

Sample	C at 0.2 A g ⁻¹ (F g ⁻¹)	S _{BET} (m ² g ⁻¹)	N (wt.%)	O (wt.%)	C _s (μF cm ⁻²)
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SC-AC-02	310	1402	< 0.3	6.6	22.1
SC-AC-02/450NH₃	307	1136	2.8	2.4	27.0
SC-AC-09	322	2306	< 0.3	5.8	14.1
SC-AC-09-400NH₃	295	2205	2.4	3.6	13.4
SC-AC-09-450NH₃	307	2237	2.5	2.1	13.7
SC-AC-09-500NH₃	292	2171	3.0	2.4	13.5
SC-AC-09-680NH₃	285	2127	3.2	1.1	13.4
SC-AC-09-HT150N	283	2040	5.2	6.0	13.9
SC-AC-09-HT180N	291	2070	4.8	5.8	14.1
SC-AC-09-350U	248	1500	11.5	8.5	16.6
SC-AC-09-450U	278	1780	8.0	6.4	15.7
SC-AC-09-550U	293	2080	4.3	3.1	14.1
SC-AC-09-650U	282	1960	4.5	3.8	14.4
SC-AC-10	328	2630	< 0.3	8.0	12.5
SC-AC-10-450NH₃	330	2560	3.1	4.1	12.9
SC-AC-11	331	2830	< 0.3	5.9	11.7
SC-AC-11-450NH₃	335	2770			12.1
P27-AC/800-3	299	2020	< 0.3	4.2	14.8
P27-AC/800-3-500/2 NH₃	258	1820	2.6	2.1	14.2

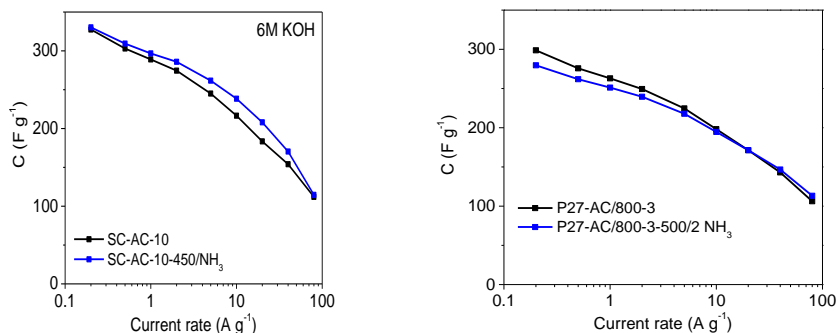


Figure 6.4 Specific capacitance at different current rates of pristine and ammonia treated SC-AC-10 and P27-AC/800-3 activated carbons.

Much higher nitrogen was incorporated in the carbon surface when AC was treated with ammonia under hydrothermal conditions. The nitrogen content in the resultant N-ACs was approximately 5 wt. % regardless of the process temperature in the range of 150-180 °C. Moreover, enrichment in the nitrogen was not accompanied by decrease in the oxygen content. A significant increase in the C-OH group and a decrease in the COOH group were observed due to the applied treatment as proven by XPS study (Table 7.3, WP7). As a result, a high contribution of pseudocapacitance was recorded. Finally, only a slight drop of gravimetric capacity occurs despite BET surface area decreasing by 10-12 %.

All urea-treated materials show a much lower gravimetric capacitance than the pristine SC-AC-09 activated carbon (248-293 F g⁻¹ vs. 322 F g⁻¹). The negative impact of urea treatment can be related to a drastic drop of the specific surface area of the modified ACs by 20-35 %. However, the high amount of nitrogen introduced to the AC structure (4-12 wt. %) causes a higher contribution of pseudocapacitance, as suggested by the higher values of the specific surface capacitance. This finding can be explained by much higher amount of electrochemically active C=O and C-OH groups and pyridinic nitrogen revealed by XPS study (Table 7.4, WP7). Unfortunately, the benefit from the presence of heteroatoms is hidden by a decrease of the BET surface area.

Figure 6.5 shows the relationship between the specific surface capacitance and the heteroatoms content (O+N) for all modified ACs, including the oxidized and nitrogen-doped ACs. A linear correlation was obtained with a coefficient factor R² of 0.88. These results allow concluding that both the oxygen and nitrogen functionalities are responsible to the same extent for pseudocapacitance effect of ACs.

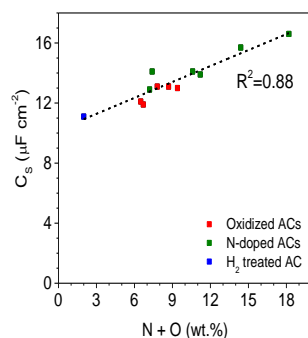


Figure 6.5 Specific surface capacitance vs. heteroatoms content of the modified ACs

Asymmetric capacitor

Basic electrochemical characterization of ACs in a 3-electrode cell does not give any evident prove that different surface chemistry and pore size distribution influence on the width of potential window (over-potential of water decomposition). This is true in case of KOH and Na₂SO₄ as an electrolyte and, for both the positive and negative electrodes. For this reason, when choosing material for the electrodes of capacitor, only the high gravimetric capacity measured in the operating conditions of the target asymmetric capacitor was considered.

Unmodified SC-AC-11 was selected as an active material of negative electrode, as this AC shows the highest capacitance. Moreover, high micropore volume seems to be beneficial for effective reversible hydrogen storage, derived from eventual water decomposition. Among ACs studied SC-AC-11 exhibits the highest micropore volume (0.92 cm³ g⁻¹). SC-AC-10-300/0.5 air was selected as positive electrode. The mild oxidation did not cause a significant BET surface reducing which allowed keeping sufficient specific capacity. Moreover, this AC shows improved rate capability in contrast to the parent material.

Several systematical tests of asymmetric capacitor in 3-electrode cell indicated that an optimal mass ratio of positive/negative electrode is in the range of 1.1-1.4 and 2.3-2.6, in 0.5 M Na₂SO₄ and 6 M KOH electrolyte, respectively. Moreover, a work potential window can be significantly wider then thermodynamic value of 1.12 V thanks to over-potential of water decomposition on the negative electrode.

The cyclability of selected asymmetric capacitor at a charge/discharge current density of 2 A g⁻¹ (per average mass of active material) is shown in Figure 6.6.

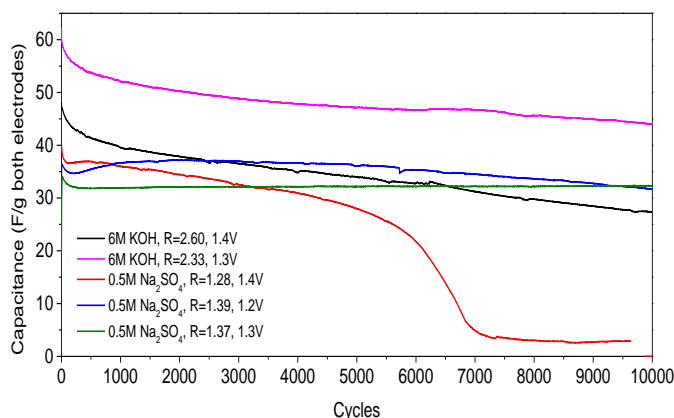


Figure 6.6 Cyclability of selected asymmetric capacitors. Capacitance related to the total mass of both electrodes (including carbon black and binder)

Both capacitors operated in 6M KOH as an electrolyte have poor cycling stability. After 10000 charge/discharge cycles, they lost about 40 % of the initial capacity. The device with a neutral electrolyte charged up to 1.4 V also does not work properly. A sharp capacity drop after 5000 cycles can be related to electrolyte decomposition and an increase of pressure inside the cell. The Na_2SO_4 -based capacitor rated at 1.3 V is the most stable up to 10 000 cycles, maintaining about 95 % of the initial capacity. The long-term specific capacity and energy of this system can be estimated as 32 F g^{-1} and 7.5 Wh kg^{-1} , respectively.

AC/G composite as an electrode for supercapacitors

Two AC/G composites ([SC-AC-11/GO-05]-TR700 and [SC-AC-11/GO-05]-HT180) were provided by INCAR-CSIC for their evaluation as electrodes for supercapacitors operating in aqueous electrolytes. The electrochemical performance of the composites was determined by cyclic voltammetry and galvanostatic charge-discharge measurements, similarly to the characterization of the oxidized and nitrogen-doped ACs (Task 3.3 and 3.4). A 6 M KOH solution was used as an electrolyte.

Both AC/G composites show significantly lower gravimetric capacitance than the parent AC. Undoubtedly, it is related to a decrease in the BET surface area (Table 6.4). Despite the significantly lower S_{BET} [SC-AC-11/GO-05]-HT180 exhibits much better electrochemical performance than [SC-AC-11/GO-05]-TR700. Distinct redox humps are visible on the CV curve at 2 mV s^{-1} (Figure 6.7 a), which confirms a high contribution of the pseudocapacitance in the overall gravimetric capacitance of [SC-AC-11/GO-05]-HT180.

Table 6.4 Gravimetric capacitance, specific surface area, oxygen content and specific surface capacity of SC-AC-11 and SC-AC-11/G composites

Sample	C at 0.2 A g^{-1} (F g^{-1})	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	O (wt.%)	C_s ($\mu\text{F cm}^{-2}$)
SC-AC-11	331	2830	5.9	11.7
[SC-AC-11/GO-05]-TR700	220	1934	2.2	10.7
[SC-AC-11/GO-05]-HT180	287	1615	6.6	18.3

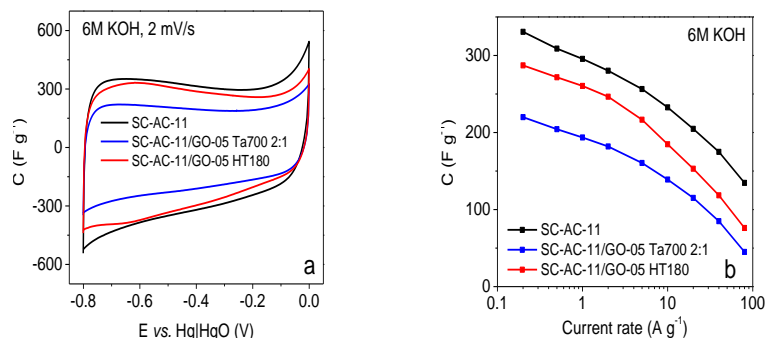


Figure 6.7 Electrochemical behavior of SC-AC-11 and SC-AC-11/G composites.

The effect is not observed for the composite containing thermally reduced GO-05 [SC-AC-11/GO-05]-TR700. A relatively high specific surface capacitance of [SC-AC-11/GO-05]-HT180 ($18.3 \mu\text{F cm}^{-2}$) is probably caused by a high amount of oxygen introduced by hydrothermally reduced GO-05. Despite the presence of the well-conducting graphene phase, the performance of both composites at high current rate is only moderate (Figure 6.7 b) and worse than that of SC-AC-11.

Task 6.2 Testing of active electrode materials in hybrid energy storage systems operating in aqueous redox electrolytes (INCAR-CSIC)

As a preliminary step in the development of hybrid energy storage systems operating in aqueous redox electrolytes, a screening of the electrochemical performance of the most representative ACs, Gs and AC/Gs obtained in previous WPs was carried out. With this aim, symmetric devices were firstly set up. At this point it is important to remember that in the hybrid systems one of the two electrodes acts as a battery-type electrode (development of a faradaic reaction) while the other one acts as a capacitor-type electrode (formation of the electrical double layer). Bearing this in mind the required materials have to mainly present high electrical conductivities and suitable textural characteristics, respectively.

The disk-shaped AC, AC/G or Gs electrodes (geometric area $\approx 1.13 \text{ cm}^2$, weight = 30 mg) were prepared by mixing the corresponding material with 10 and 25 wt. % PVDF as binder, respectively (otherwise stated). A solution of 1.0 M H_2SO_4 was used as supporting electrolyte.

The cell voltage profiles and the potential evolution of each electrode during the galvanostatic cycling of the symmetric devices were simultaneously monitored by performing synchronous cyclic chronopotentiometric tests (at 1.0 V by applying increasing current values between 1-125 mA) in a "T-type" Swagelok® cell using a 2-3 electrode configuration. To obtain this configuration a two-electrode cell was assembled and at the third-end connection an Ag/AgCl/3.5 M KCl reference electrode (0.205 V vs. NHE) was incorporated, making it possible to determine the potential at which each electrode was operating when the cell voltage was applied. The cell capacitance values were calculated from the constant current discharge profiles (avoiding the ohmic drop).

Symmetric Devices

- Activated carbons (ACs):

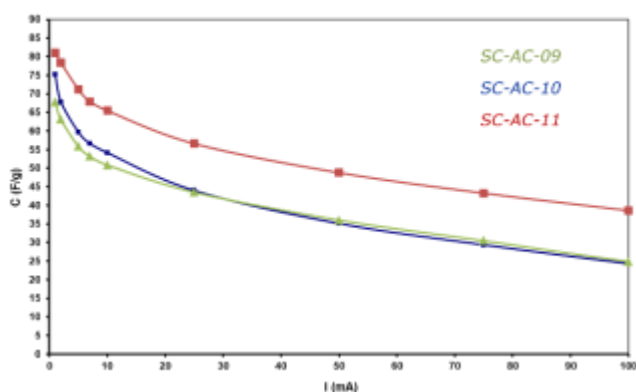


Figure 6.8 Evolution of the specific capacitance of the symmetric cells with ACs from conventional and microwave technology

As previously stated, the main aim of these tests was to compare the electrochemical performance of ACs obtained by a conventional activation method but starting from different precursors (derived from conventional and microwave technology). SC-AC-02 was discarded as it exhibited poor textural properties (mainly a low specific surface area).

As it can be seen in Figure 6.8, at all the constant currents applied, the C values of the SC-AC-11 symmetric cell were markedly higher than those calculated for SC-AC-09 and SC-AC-10 (65 vs 54 and 50 $F\ g^{-1}$ at 0.2 $A\ g^{-1}$, respectively). Moreover, the capacitance decreases at increased currents applied is also lower in the system using SC-AC-11 as anode/cathode (52 % vs 68 % for the two other devices). These results (Table 6.5) agreed with the textural and chemical characteristics previously described for the different activated carbons evaluated (SC-AC-11 showed a higher S_{BET} value and lower oxygen content than SC-AC-10, for example). Thus, the microwave derived AC seemed to be a promising material to be used as capacitor-type electrode in the hybrid devices showing improved properties when comparing to the activated carbons from the conventional technology. At this point is important to remark that, as described above, the energy consumption to obtain the microwave precursors is markedly lower when comparing with the conventional technology, thus representing a significant step forward in the search of more effective carbon precursors.

Table 6.5 Comparison of the electrochemical performance of symmetric devices assembled (in H_2SO_4) with the different ACs synthesized (from conventional and microwave technologies)

Device	$C\ (F\ g^{-1})$ (at 0.2 $A\ g^{-1}$)	$E\ (W\ h\ Kg^{-1})$
SC-AC-09_SIM	50.0	7.1
SC-AC-10_SIM	51.1	7.4
SC-AC-11_SIM	65.4	9.0

- Graphene materials (Gs):

As previously mentioned the graphene materials synthesized were mainly investigated to be used as battery-type electrodes in the hybrid materials (according to their textural and chemical characteristics). Remembering, some of the previously described materials (i.e. SC-TRG01-700 and SC-TRG01-1000), obtained from conventional carbon precursors, showed an appropriate performance. The main goal of the tests here described has been to compare the electrochemical behavior of those Gs with the obtained from microwave derived carbon precursors (CTR series).

With this aim different symmetric devices (in H_2SO_4 1M) were assembled by using the different conventional and microwave-derived graphene materials. Figure 6.9 shows the comparative of the results obtained regarding the evolution of the C values of the systems evaluated when increasing constant currents applied.

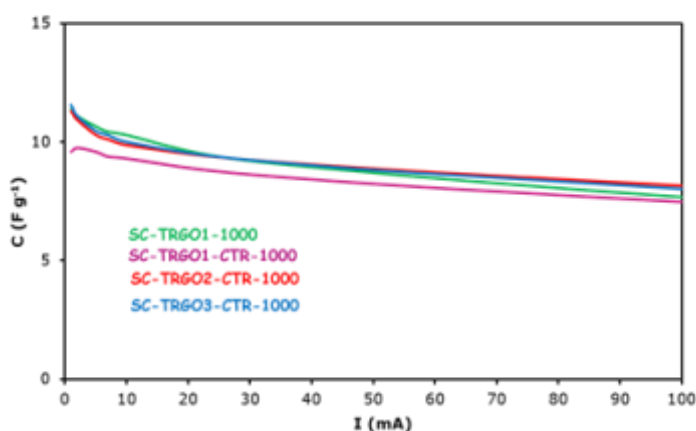


Figure 6.9 Evolution on the specific capacitance values of the symmetric cells set up with graphene materials derived from conventional and microwave technologies

According to the obtained results it can be concluded that the graphene materials from the microwave derived precursors exhibited an electrochemical performance similar to that of the

conventional ones (Table 6.6). The obtained data, in terms of C and E values, are very good as they allow concluding that the new microwave technology, with lower time and energy consumptions when synthesizing the carbon precursors, results in similar graphene materials (to those obtained from conventional precursors) to be used in the electrochemical devices under study. It is important to remark that both capacitance and energy density values of these investigated symmetric devices are very low, but these graphene materials are not thought to be used as capacitor-like electrodes but as battery-type, as stated before.

Table 6.6 Comparison of the electrochemical performance of symmetric devices assembled (in H_2SO_4) with the different graphene materials synthesized (from conventional and microwave technologies)

Electrode material	O (wt. %)	S_{BET} ($m^2 g^{-1}$)	C ($F g^{-1}$) at $0.2 A g^{-1}$	E ($W h Kg^{-1}$)
SC-TRGO1-1000	1.3	477	10	1.4
SC-TRGO1-CTR-1000	0.4	422	9	1.3
SC-TRGO2-CTR-1000	0.8	492	10	1.4
SC-TRGO3-CTR-1000	0.8	490	10	1.4

- Composite materials (AC/G):

Following with the electrochemical characterization of the different materials synthesized, also the composite materials (AC/G) were evaluated following the same procedure previously described. Thus, symmetric devices were set up using an acidic medium as electrolyte (Figure 6.10).

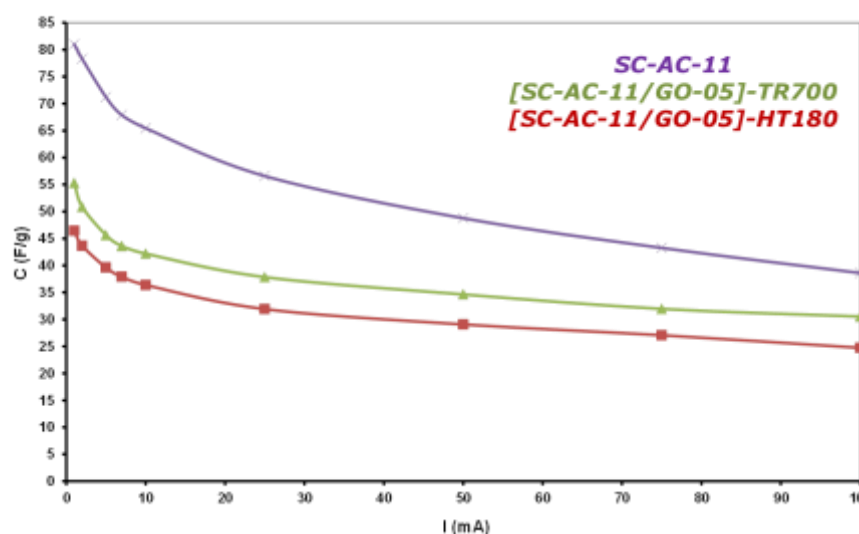


Figure 6.10 Evolution on the specific capacitance values of the symmetric cells set up with composite materials

As it can be seen, and when comparing with the electrochemical performance of the symmetric device set up using SC-AC-11 (which has been included with comparative purposes) both composite materials presented lower performances in terms of capacitance and energy density values (Table 6.7)

Table 6.7 Comparison of the electrochemical performance of symmetric devices assembled (in H_2SO_4) with different composite materials

Electrode material	$C (F g^{-1})$ at $0.2 A g^{-1}$	$E (W h Kg^{-1})$
SC-AC-11	65.4	9.0
[SC-AC-11/GO-05]TR700	46.2	6.0
[SC-AC-11/GO-05]TR700	36.4	5.0

These results were in agreement with the decrease in the specific surface areas measured in the AC/Gs from the two synthesis procedures followed (when comparing with the starting activated carbon) and confirmed the intimate contact between the graphene layers and the AC particles. However, they both exhibited an improved rate capability as the capacitance drop was lower at increasing current densities. This result allowed us to think about these materials not as suitable capacitor-like but as battery-type electrodes.

Asymmetric/Hybrid Devices

Different experiments were carried out after assembling asymmetric/hybrid devices. With comparative purposes, firstly it was evaluated the electrochemical performance of asymmetric devices in the supporting electrolyte (H_2SO_4) selecting SC-AC-11 as the capacitor-like electrode and SC-TRGO1-1000 as battery-like electrode (Figure 6.11). Also, the data corresponding to the respective symmetric devices have been included in the figure.

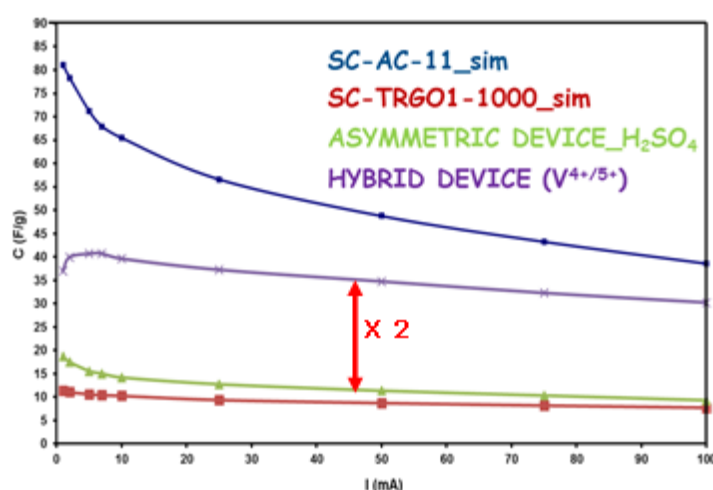


Figure 6.11 Evolution on the specific capacitance values of the symmetric, asymmetric and hybrid cells

As expected, the asymmetric device in the supporting electrolyte slightly improved the C value of the symmetric one assembled with the graphene material. However, such capacitance resulted considerably lower than the corresponding to the system with SC-AC-11 (which was explained considering the poor textural properties of the SC-TRGO1-1000) (Table 6.8).

Table 6.8 Comparison of the electrochemical performance of the different devices assembled using SC-AC-11 and/or SC-TRGO1-1000 in symmetric, asymmetric and hybrid devices

Device	C ($F g^{-1}$)	E ($W h Kg^{-1}$)
SC-AC-11_SIM	81-39	11.2-4.5
SC-TRGO1-1000_SIM	11-7	1.6-1.0
ASYMMETRIC DEVICE_H₂SO₄	19-9	2.6-1.0
HYBRID DEVICE (V^{4+/5+})	37-30	5.1-4.0

The next step was the evaluation of a real asymmetric/hybrid device. The experimental set up was slightly different to the previous ones because a Nafion[®] membrane was introduced in the 2-3 electrodes cell to separate the two half-cells as two different electrolytes were used:

- A H₂SO₄ 1.0 M solution in the negative half-cell (SC-AC-11 as electrode)
- A VOSO₄ 0.5M / H₂SO₄ 1.0 M solution in the positive half-cell (SC-TRGO1-1000 as electrode)

Thus, the system was asymmetric as different electrode materials were used in the two half-cells of the whole device and hybrid as the energy storage mechanisms of each one of them were different (one of the electrodes where the V^{4+/5+} redox reactions occur acts as a battery-type electrode, while the other retains its capacitor-type behaviour).

After developing the corresponding charge/discharge experiments, the C and E values of this device resulted to be significantly improved with respect to the other systems evaluated, being approximately double that of the asymmetric one. Moreover, the decrease in both parameters at increasing current densities applied was lower thus representing an enhancement of the electrochemical performance. These promising results offer the possibility of continuing with the development of hybrid devices in the search of higher capacitance and, mainly, energy density values. For this purpose, the graphene materials derived from the microwave precursors could be a promising alternative. Also, other electroactive inorganic and/or organic species could be evaluated.

Work Package conclusions:

- Surface functionalities have a significant impact on the capacity performance of ACs in aqueous electrolyte, which is related to pseudocapacitance effect and better electrolyte wettability. However, a specific surface area of the material is still a key factor and must be retained to high extent to ensure enough overall specific capacity of AC. The total oxygen content should not exceed about 18 wt. % to avoid the negative effect of inter-particle resistance. Both the oxygen and nitrogen functionalities are responsible to the same extent for pseudocapacitance effect of ACs, however, some kind of species, like C=O, C-OH and pyridinic nitrogen, seem to be slightly more electrochemically active. Asymmetric capacitor builds of SC-AC-11 as negative electrode and SC-AC-10-300/0.5 air as positive electrode can work stable in 0.5 M Na₂SO₄ up to 1.3 V.

The electrochemical performance of AC/rGO composite is worse than the bare AC. The drop of specific surface area of the composite is very large and cannot be balanced by pseudocapacitance derived from rGO component.

- Several materials from conventional and microwave-derived precursors are available to be used as suitable electrodes in symmetric, asymmetric and hybrid devices. More importantly, the materials from the microwave technology, both ACs and TRGOs exhibit electrochemical performances comparable or even better to those obtained from conventional precursors but with significant lower energy consumption in their synthesis procedure.

- Composite materials AC/G, starting from activated carbons and graphene precursors, appear to be promising materials in electrochemical devices combining both the proper specific surface area of ACs and the high electrical conductivity of Gs. The hydrothermal route, offering a structure of graphene layers wrapping the AC particles, represents a promising methodology in the search of more effective active materials.

- The asymmetric/hybrid devices, combining different active electrode materials and energy storage mechanisms (both the formation of the electrical double layer in the capacitor-type

electrode and the development of faradaic reactions in the battery-type electrode) significantly increase the energy density values of similar systems in the supporting electrolyte.

WP7. ADVANCED CHARACTERIZATION OF THE COAL-LIQUID BASED CARBON MATERIALS (UEA)

Task 7.1 Advanced characterization of the synthesized activated carbons (ACs) (UEA)

UEA received 4 ACs for characterisation, labelled as SC-AC-02, SC-AC-09, SC-AC-10 and SC-AC-11. The first 3 ACs were conventionally synthesised from anthracene oil derived green cokes obtained at different temperatures. SC-AC-11 is a non-conventional AC obtained from microwaved precursors. All of them, except SC-AC-02, show an adequate morphology as suitable active electrode materials for supercapacitors (Figure 7.1).

According to the nitrogen adsorption results, the produced activated carbons are mainly microporous materials. As suggested by means of SEM and N₂ adsorption at -196.1 °C, the specific surface area of SC-AC-02 is too low for a good electrode material (Table 7.1). SC-AC-11, however, shows a significant specific surface area, achieving 2871 m² g⁻¹ and a total pore volume of 1.52 cm³ g⁻¹. In addition, this sample presents the lowest oxygen content (4.7 wt. %) (Table 7.1).

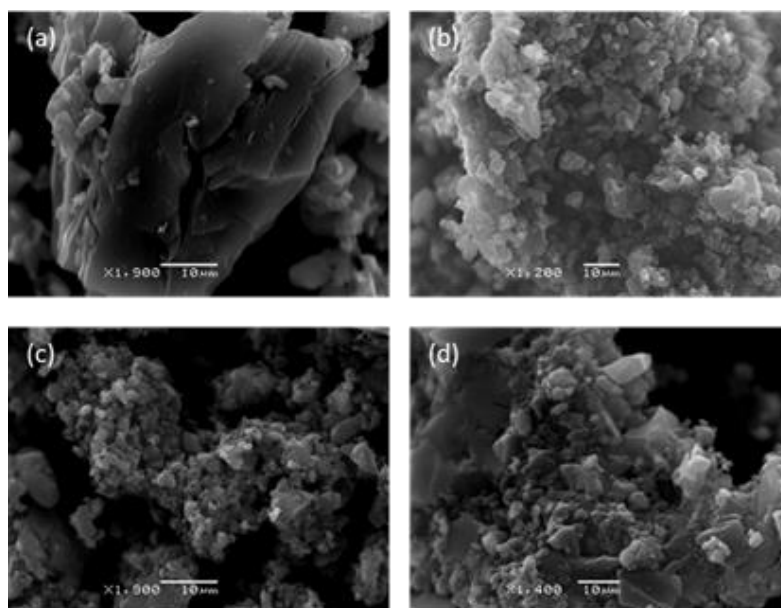


Figure 7.1 SEM micrograph of the ACs obtained from different precursors: (a) SC-AC-02 (b) SC-AC-09 (c) SC-AC-10 and (d) SC-AC-11

Table 7.1 Elemental analysis and physical properties deduced from N₂ adsorption at -196.1 °C of the synthesised activated carbons

Sample	Elemental analysis (wt.%)					Nitrogen adsorption at -196.1 °C			
	C	H	N	S	O	S _{BET} (m ² g ⁻¹)	V _T (cm ³ g ⁻¹) at P/P ₀ =0.965	V _{micro} (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)
SC-AC-02	92.7	0.6	0.3	0.0	6.4	1291	0.58	0.50	0.08
SC-AC-09	92.9	0.5	0.2	0.0	6.4	2131	0.90	0.80	0.10
SC-AC-10	92.1	0.4	0.3	0.0	7.2	2458	1.10	0.88	0.22
SC-AC-11	94.6	0.5	0.2	0.0	4.7	2871	1.52	0.93	0.59

Wide-scan spectra in the binding energy range of approximately 01000 eV was obtained to identify the elements present on the surface of the synthesised activated carbons and to perform a quantitative analysis. The elements detected were carbon and oxygen, being carbon the most abundant. SC-AC-11 presents a greater Csp² content and C/O ratio (Table 7.2), much higher than that of other ACs synthesised from AO, being this result in agreement with the elemental analysis shown in Table 7.1.

To further analyse the surface chemical composition, the C(1s) peak was curve-fitted, emerging five peaks at different binding energies (B.E.), which correspond to C graphitic (BE = 284.3284.4 eV), C-O in the hydroxyl bond (BE = 285.6285.7 eV), C=O in the carbonyl bond (BE = 286.9-

287.0) and the peak at around 288.9 assigned to the carboxyl bond. The $\pi \rightarrow \pi^*$ shake-up signal (290.8 eV) typical for sp^2 - hybridized carbon was also found (Table 7.2).

Although ACs have been synthesised from different precursors, the activation process was carried out under the same conditions. Consequently, the surface composition derived from the high-resolution spectra of C(1s) is relatively like previous samples. A slightly higher graphitic content and lower percentage of carbonyl groups were found in SC-AC-11 in comparison to other specimens.

From these results, we can conclude that microwave technology has the potential to produce activated carbons with high surface area and appropriate properties to be excellent materials for electrodes in supercapacitors.

Table 7.2 Surface composition of the ACs and residual oxygen functional groups by curve fitting of C(1s) spectra

SAMPLE	C (at.%)	O (at.%)	C/O	C-C	C-OH/ C-O-C	C=O	C(O)OH	$\pi \rightarrow \pi^*$
SC-AC-02	87.7	12.3	7.1	60.1	16.5	7.6	7.3	8.6
SC-AC-09	91.7	8.3	11.0	61.1	14.8	8.0	8.4	7.6
SC-AC-10	91.1	8.9	10.2	64.1	15.0	7.3	8.9	4.6
SC-AC-11	93.6	6.4	14.6	65.2	15.8	7.1	8.9	3.0

Ten modified ACs from SC-AC-09, SC-AC-10 and SC-AC-11 have been received at UEA from TUWRO to characterise their surface chemistry. They were subjected to different treatments (acid, air, hydrogen and ammonium persulfate) with the aim of modifying their oxygen-containing functional groups.

UEA carried out the infrared spectra and XPS analysis of these materials. The infrared spectra of the modified activated carbons show the presence of the bending O-H bond from carboxyl and hydroxyl groups, the band of C=O from carbonyl and carboxyl groups, as well as the bending C-O of carboxyl and the C-O-C stretching vibration of epoxy group (Figure 7.2). AC-10-700H presents less pronounced bands.

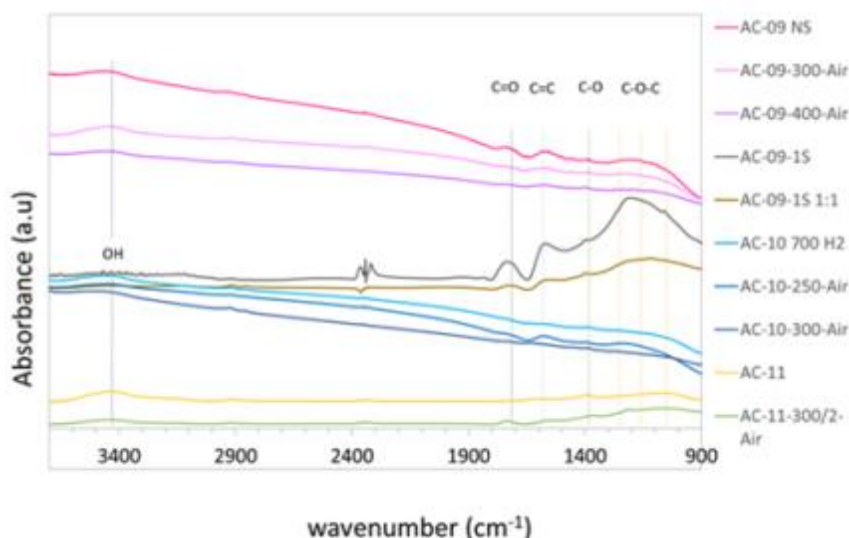


Figure 7.2 FTIR spectra of the modified ACs with oxygen functionalities

Wide-scan spectra in the binding energy range of approximately 01000 eV was obtained to identify the elements present on the activated carbon surfaces and to perform a quantitative analysis. The main elements detected in the modified ACs were carbon and oxygen, being carbon the most abundant (Table 7.3).

The three approaches were able to incorporate oxygen functionalities on the surface of the ACs. The oxidations carried out with ammonium persulfate achieved a significant incorporation of oxygen functionalities, showing SC-AC-09-1S and SC-AC-09-1S 1:1 the lowest C/O ratios, 4.4 and 5.6 respectively (Table 7.3). The acid method is also very effective, being 6.3 the C/O ratio achieved by AC-09 NS.

It is worthy to mention that the three ACs were subject to the air treatment at 300 °C. This modification accomplished a 14.4 % increase in the oxygen content of SC-AC-09-300 Air in

comparison to the parent activated carbon, a 7.8 % rise in SC-AC-10-300 Air and 18.7 % in SC-AC-11-300/2 Air, evidencing their different reactivity towards air.

The type of functionality is very much dependent on the modification carried out. The acid treatment and the modification with concentrated ammonium persulfate seem to promote the integration of carboxyl functionalities in higher degree than air. The presence of carboxyl groups increased 58.3 % in SC-AC-09-NS and 90.5 % in SC-AC-09-1S. However, reactions with air raise the presence of C-O bonds in hydroxyl and epoxy groups, especially at higher temperatures.

The oxidation carried out with ammonium persulfate and water (SC-AC-09-1S 1:1) appears to be the most promising method to incorporate a wider range of functionalities. This treatment is the most successful including C-O bonds (rise of 33.1 %) but also achieved a significantly good incorporation of carboxyl groups (41.7 % of increase).

Table 7.3 Surface composition of the modified ACs with oxygen functionalities

SAMPLE	XPS								
	C (at.%)	O (at.%)	N (at.%)	C/O	C -C	C-OH/ C-O-C	C=O	C(O)OH	$\pi \rightarrow \pi^*$
SC-AC-09	91.7	8.3	---	11.0	61.1	14.8	8.0	8.4	7.6
SC-AC-09 300 Air	90.5	9.5	---	9.5	58.4	16.7	7.2	9.8	8.0
SC-AC-09 400 Air	90.0	10.0	---	9.0	57.5	17.9	9.4	9.2	6.1
SC-AC-09 NS	85.9	13.6	0.4	6.3	58.2	15.5	6.8	13.3	6.2
SC-AC-09-1S	81.5	18.5	---	4.4	60.4	15.6	4.2	16.0	3.8
SC-AC-09-1S 1:1	84.8	15.2	---	5.6	61.1	19.7	3.6	11.9	3.8
SC-AC-10	91.1	8.9	---	10.2	64.1	15.0	7.3	8.9	4.6
SC-AC-10 250 Air	89.6	10.4	---	8.6	59.7	16.7	7.5	10.4	5.7
SC-AC-10 300 Air	90.4	9.6	---	9.4	59.0	17.0	8.4	10.8	4.7
SC-AC-10 700 H ₂	95.9	4.1	---	23.4	66.3	12.1	7.5	8.6	5.5
SC-AC-11	93.6	6.4	---	14.6	65.2	15.8	7.1	8.9	3.0
SC-AC-11 300/2 Air	92.4	7.6	---	12.2	59.0	18.5	7.2	11.4	3.9
SC-AC-11 350/0.5 Air	89.0	11.0	---	8.1	59.0	19.8	7.0	11.1	3.2

Heat treatment of SC-AC-10 in a hydrogen flow at 700 °C (SC-AC-10-700H) led to a significant removal of oxygen, which is reflected in a greater C/O ratio (23.4) estimated by XPS, a higher percentage of graphitic carbon and lower percentage of C-O bonds in hydroxyl and epoxy functionalities (Table 7.3) in comparison with the parent activated carbon (SC-AC-10).

Thirteen activated carbons have been also received from TUWRO to characterise the surface chemistry after some amendments on their nitrogen functional group distribution. The starting materials (SC-AC-09, SC-AC-10 and SC-AC-11) have been modified with the goal of introducing nitrogen functionalities, principally pyridine and pyrrolic nitrogen.

SC-AC-09-400 NH₃, SC-AC-09-450 NH₃, SC-AC-10-450 NH₃, SC-AC-11-450 NH₃ and SC-AC-09-500 NH₃ were obtained by ammonia treatment at 400, 450 and 500 °C, respectively. SC-AC-09 was also hydrothermally treated at 120, 150 and 180 °C, obtaining the materials SC-AC09-HT120N, SC-AC-09-HT150N and SC-AC-09-HT180N. Finally, SC-AC-09-350U, SC-AC-09-400U, SC-AC-09-450U, SC-AC-09-550U and SC-AC-09-650U reacted with urea at 350, 400, 450, 550 and 650 °C for 1 h.

UEA carried out the corresponding FTIR and XPS analysis. Besides the presence of O-H bond from carboxyl and hydroxyl groups, C=O from carbonyl and carboxyl groups, C-O from carboxyl as well as the C-O-C stretching vibration of epoxy group, the bending of C-N=C and C-N bonds is also noticed in these materials (Figure 7.3).

The three approaches performed have been able to incorporate nitrogen on the surface of the activated carbons (Table 7.4). The modification with urea at the lowest temperature (350 °C) appears to be the most effective method for the inclusion of nitrogen functionalities, with 8.7 at. % of nitrogen content detected on the surface of this activated carbon. With increasing temperatures, the presence of nitrogen drops to approximately 6.5 at. % at temperatures between 400 and 450 °C, to 5.1at. % at 550 °C and just 3.8 at. % when the urea treatment is carried out at 650 °C.

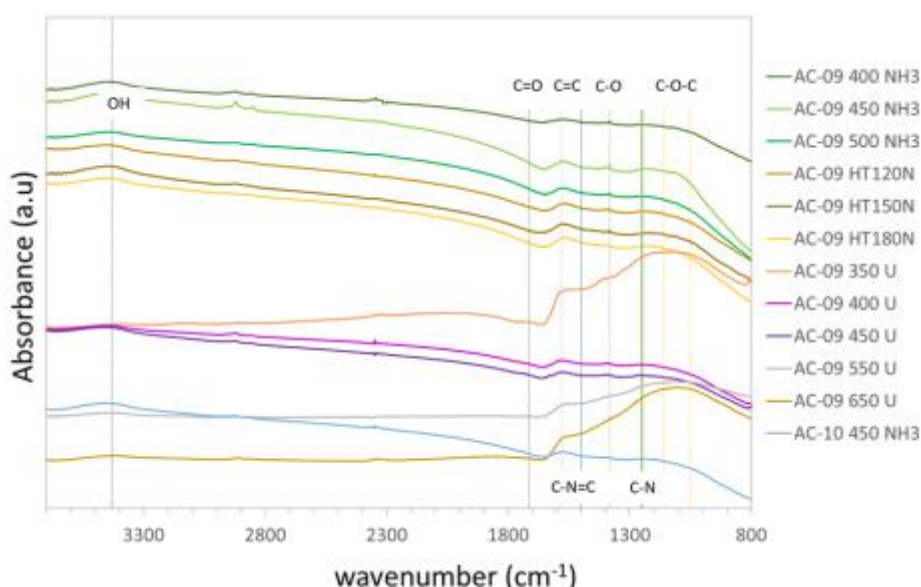


Figure 7.3 FTIR spectra of the modified ACs with nitrogen functionalities

Table 7.4 Surface composition of the modified ACs with nitrogen functionalities

SAMPLE	XPS									
	C (at.%)	O (at.%)	N (at.%)	C/O	C/N	C -C	C-OH/ C-O-C/ C=N	C=O/ C-N	C(O)OH	n→n*
SC-AC-09	91.7	8.3	---	11.0	---	61.1	14.8	8.0	8.4	7.6
SC-AC-09 NH3 400	92.2	4.1	3.8	22.5	24.3	59.3	16.7	10.9	5.6	7.6
SC-AC-09 NH3 450	93.1	3.8	3.2	24.5	29.1	60.4	16.1	11.6	4.5	7.4
SC-AC-09 NH3 500	93.6	2.9	3.6	32.3	26.0	61.5	15.2	12.5	3.4	7.3
SC-AC-09 HT 120N	88.8	8.2	3.0	10.8	29.6	56.7	19.5	8.8	7.8	7.2
SC-AC-09 HT 150 N	85.6	9.3	5.1	9.2	16.8	53.3	23.8	10.3	5.6	7.0
SC-AC-09 HT 180 N	88.5	7.1	4.4	12.5	20.1	57.0	20.7	9.9	4.7	7.7
SC-AC-09 350U	84.6	6.7	8.7	12.6	9.7	56.5	19.9	12.6	6.8	4.3
SC-AC-09 400U	87.0	6.7	6.3	13.0	13.8	56.2	18.5	11.6	7.2	6.5
SC-AC-09 450U	86.4	7.0	6.6	12.3	13.1	55.1	19.2	14.2	5.8	5.7
SC-AC-09 550U	90.4	4.5	5.1	20.1	17.7	59.4	18.9	9.1	5.7	7.0
SC-AC-09 650U	90.6	5.6	3.8	16.2	23.8	59.4	18.3	8.9	5.5	7.9
SC-AC-10	91.1	8.9	---	10.2	---	64.1	15.0	7.3	8.9	4.6
SC-AC-10 NH3 450	91.4	5.1	3.5	17.9	26.1	60.1	16.3	9.6	6.5	7.4
SC-AC-11	93.6	6.4	---	14.6	---	65.2	15.8	7.1	8.9	3.0
SC-AC-11 NH3 450	92.7	5.2	2.1	17.8	44.1	59.7	17.3	12.4	4.1	6.6

The hydrothermal method is able to incorporate up to 5.1 at. % of nitrogen at 150 °C, which seems to be the optimal temperature. Finally, ammonia treatment increased the nitrogen content in roughly 3.5 at. %, regardless the temperature at which the reaction was performed. The three ACs were subject to the ammonia treatment at 450 °C, in this case they show a very similar reactivity towards nitrogen.

Urea modification at temperatures up to 450 °C and hydrothermal procedure have had a marginal impact on the oxygen content on the surface of the ACs, however urea at temperatures equal or greater than 550 °C and ammonia have caused a significant removal of oxygen accelerated in the latter by the reductive atmosphere of amination, especially at 500 °C.

To analyse the surface in more detail, high resolution C (1s) spectra were obtained and the carbon spectra were fitted using GaussianLorentzian peaks. Due to the overlap of oxygen and nitrogen functionalities at similar binding energies, it is not easy to establish conclusions (Table 7.4). The three methodologies instigate a reduction in the percentage of graphitic carbon and carboxyl bonds. Nevertheless, ammonia promotes in higher degree the introduction of C=O and C-N bonds, while the hydrothermal treatment favours the formation of C-O and C=N bonds. Urea is able to increase both types of functionalities, especially at temperatures up to 450 °C.

The N(1s) peak was also curve-fitted (Table 7.5), emerging five peaks at different binding energies (BE), which correspond to N6 from N-pyridine like structures (BE = 398.8-398.4 eV), NC from amides/amines or lactams (BE = 399.9-399.5 eV), N5 from N-pyrrolic (BE = 400.6-400.0 eV), NQ from N-quaternary (BE=401.8-400.9) and the peak at around 405-402 eV assigned to the nitrogen oxides as Pyridine N-Oxide (N-X).

Good introduction of pyridine nitrogen (N6) has been achieved by the three approaches, particularly with ammonia and urea reactions at temperatures up to 450 °C (Table 7.5). Ammonia at 400 and 450 °C and, hydrothermal treatment (especially at 180 °C) are effective introducing amides/amines or lactams (N-C). Urea treatment performed at temperatures up to 450 °C does not seem as active promoting the presence of these groups. However, substantial percentages of pyrrolic nitrogen (N5) have been identified on the surface of these samples (Table 7.5).

Table 7.5 Parameters derived from the curve fitting of N(1s) peak

	XPS				
	N6	N-C	N5	NQ	N-X
SC-AC-09 NH3 400	42.4	27.8	15.3	6.4	8.1
SC-AC-09 NH3 450	45.4	21.9	20.3	6.9	5.5
SC-AC-09 NH3 500	46.8	14.0	27.5	7.3	4.4
SC-AC-09 HT120N	39.3	24.9	20.9	7.5	7.4
SC-AC-09 HT 150 N	40.9	29.0	21.0	3.6	5.5
SC-AC-09 HT 180 N	39.1	36.4	16.0	2.6	6.0
SC-AC-09 350U	45.6	3.6	45.3	3.6	2.0
SC-AC-09 400U	44.7	6.2	42.6	4.6	2.0
SC-AC-09 450U	47.2	8.6	37.9	3.9	2.3
SC-AC-09 550U	41.2	17.7	29.6	8.7	2.7
SC-AC-09 650U	40.8	28.8	20.2	7.5	3.0
SC-AC-10 450 NH3	43.5	32.5	15.0	6.7	2.3
SC-AC-11 450 NH3	46.9	21.9	16.9	9.7	4.6

Task 7.2 Advanced characterization of the synthesized graphene materials (G) (UEA)

Twelve of the thermally reduced graphene oxides synthesized (SC-TRGOs) were received at UEA. All of them synthesised by the modified Hummers method from conventional and microwaved precursors.

Wide-scan spectra in the binding energy range of approximately 0-1000 eV were obtained to identify the elements present on the SC-TRGOs surfaces. Carbon and oxygen have been mainly detected in the wide scan spectra as shown in Table 7.6. Smaller amounts of oxygenated functional groups have been found on the surface of the graphene materials reduced at 1000 °C in comparison to those treated at 700 °C (Table 7.6), being this content lower in the unconventional samples.

Table 7.6 Surface composition of the TRGOs and residual oxygen functional groups by curve fitting of C(1s) spectra

	C (at.%)	O (at.%)	C/O	Csp ²	Csp ³	C-OH/ C-O-C	C=O	C(O)OH	n→n*
SC-TRGO1-700	90.5	9.5	9.5	64.6	12.5	9.8	2.0	3.6	7.6
SC-TRGO1-1000	97.3	2.7	36.0	67.7	14.2	6.4	1.5	2.8	7.4
SC-TRGO7-700	93.7	6.3	14.9	65.0	14.3	8.6	1.6	3.1	7.5
SC-TRGO7-1000	98.4	1.6	61.5	66.2	14.6	7.6	0.0	2.8	8.8
SC-TRGO1-CT-700	93.0	7.0	13.3	68.5	11.3	7.9	3.5	5.3	3.5
SC-TRGO1-CT-1000	97.9	2.1	46.6	70.9	10.9	6.4	2.5	4.6	4.8
SC-TRGO1-CTR-700	94.8	5.2	18.2	68.3	12.7	9.9	0.7	1.3	7.2
SC-TRGO1-CTR-1000	99.1	0.9	110.1	72.1	11.3	7.4	0.6	0.6	8.1
SC-TRGO2-CTR-700	94.1	5.9	15.9	67.8	10.6	8.7	2.8	4.4	5.6
SC-TRGO2-CTR-1000	98.1	1.9	51.6	71.5	10.3	5.8	2.3	3.5	6.6
SC-TRGO3-CTR-700	94.1	5.9	15.9	67.7	13.3	7.8	2.6	3.3	5.3
SC-TRGO3-CTR-1000	98.1	1.9	51.6	71.2	9.3	8.0	2.3	2.4	6.7

Careful curve fitting was performed on each C(1s) spectrum taking into consideration five different carbon stages and the $\pi \rightarrow \pi^*$ shake-up signal. In all the graphene materials most of the carbon atoms are sp^2 -hybridised, being this quantity higher with the increasing temperature. Unconventional materials show greater percentage of sp^2 carbon than conventional samples obtained from AO, which may be related to the lower oxygen content. All the unconventional samples reduced at 1000 °C accomplished more than 70 % of Csp^2 on their surface.

The distribution of oxygenated functionalities is relatively similar for all the samples treated at the same temperature. The origin of the detected carboxyl groups has been controversial through the course of the project, as they can be assigned to lactones or carboxylic acids. To clarify this issue and support the XPS results, temperature programmed desorption (TPD) of two conventional thermally reduced graphene oxides was carried out (Figure 7.4). The figure below shows the evolution of the CO and CO₂ for SC-TRGO1-700 and SC-TRGO1-1000

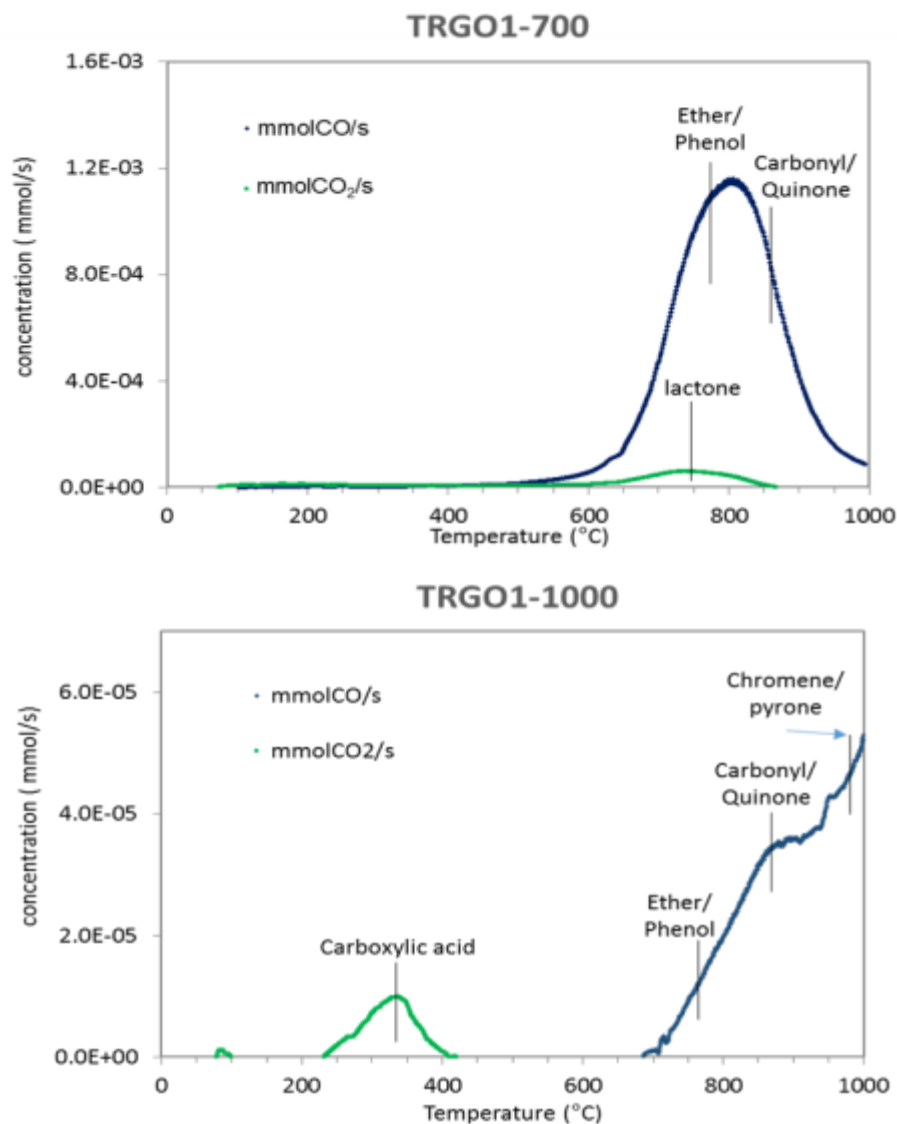


Figure 7.4 TPD of the conventional thermally reduced graphene oxides TRGO1-700 and TRGO1-1000

The CO curve of TRGO1-700 corroborates the presence of ether/phenol (600-800 °C) and carbonyl/quinone (700-950 °C) groups on the surface of the sample. On the other hand, it seems that the carboxyl groups in this material are due to the presence of lactones (600-800 °C), as suggested by the CO₂ curve (Figure 7.4).

The evolution of CO and CO₂ for SC-TRGO1-1000 shows a very low degree of functionalization. The CO curve confirms that ether/phenol (600-800 °C) and carbonyl/quinone (700-950 °C) groups are also present on the surface of the sample. Moreover, it seems that chromenes and pyrones (>950 °C) can be also found. In this case, the evolution of CO₂ verifies the existence of weak carboxylic acids, which appear between 200-450 °C (Figure 7.4). This fact can be due to secondary

reactions or radicals formed at high temperature, which have re-trapped oxygen during cooling down.

The structural differences between the synthesized graphene samples have been investigated by means of XRD and Raman spectroscopy (Table 7.7). Graphene materials obtained from microwaved precursors show very similar characteristics to those obtained by conventional means, with interlayer distances between 3.48 and 3.53.

Table 7.7 Parameters obtained by fitting of the X-Ray diffraction patterns and Raman spectra of the synthesised thermally reduced graphene oxides

Sample	XRD			Raman				
	2θ	d (Å)	Lc (nm)	G position (cm⁻¹)	D position (cm⁻¹)	HWHM G band (cm⁻¹)	HWHM D band (cm⁻¹)	I_D/I_G
SC-TRGO1-700	25.24	3.53	0.78	1590	1343	40	86	1.16
SC-TRGO1-1000	25.04	3.55	0.66	1590	1342	39	51	1.56
SC-TRGO7-700	26.27	3.39	0.71	1585	1340	38	75	1.29
SC-TRGO7-1000	26.00	3.42	1.01	1583	1337	38	49	1.44
SC-TRGO1-CT-700	25.44	3.50	0.69	1595	1345	31	47	0.97
SC-TRGO1-CT-1000	25.20	3.53	0.74	1596	1353	30	38	1.37
SC-TRGO1-CTR-700	25.37	3.51	0.74	1587	1339	41	72	0.95
SC-TRGO1-CTR-1000	25.40	3.50	0.70	1590	1340	36	57	1.19
SC-TRGO2-CTR-700	25.23	3.53	0.75	1582	1340	40	90	1.31
SC-TRGO2-CTR-1000	25.32	3.52	0.71	1583	1330	20	40	1.40
SC-TRGO3-CTR-700	25.31	3.52	0.70	1582	1340	40	90	1.32
SC-TRGO3-CTR-1000	25.36	3.51	0.71	1581	1343	20	58	1.58

Possible structural alterations and the success of the reduction process have been also investigated by means of Raman spectroscopy as it can manifest itself by the changes in relative intensities of the peaks D and G. The G band appearing between 1576 cm⁻¹ - 1596 cm⁻¹ is the most significant attributes in the Raman spectra of sp² hybridized materials. The D peak of the synthesized graphene samples is located between 1330 cm⁻¹ and 1353 cm⁻¹ corresponding to a defect-induced breathing mode of sp² rings (Table 7.7).

The honeycomb hexagonal lattice is recovered to some extent with the reduction process, being more pronounced at higher temperatures. It is observed an increase in the relative intensity ratio of D and G bands with temperature (Table 7.7). This change suggests a decrease in the average size of the sp² domains upon reduction of the exfoliated GO, which indicate that new graphitic domains were created, being smaller in size but more numerous in number.

The bandwidth of the G peak is often used as a measure of the degree of order, being in this case narrower with increasing reduction temperature (Table 7.7). Unconventional graphene materials reduced at 1000 °C show a thinner G band than the conventional ones synthesised from AO, which reinforce the potential of the microwave technology as an alternative route to produce graphene materials with similar or even improved properties in terms of surface chemistry and structure.

In addition to this, a graphene material from direct exfoliation of coal-liquid based graphites obtained by means of supercritical fluids (G-EU-01) was also characterised. SEM micrographs (Figure 7.5) show that the complete exfoliation was not accomplished, which is corroborated by means of TEM (Figure 7.6).

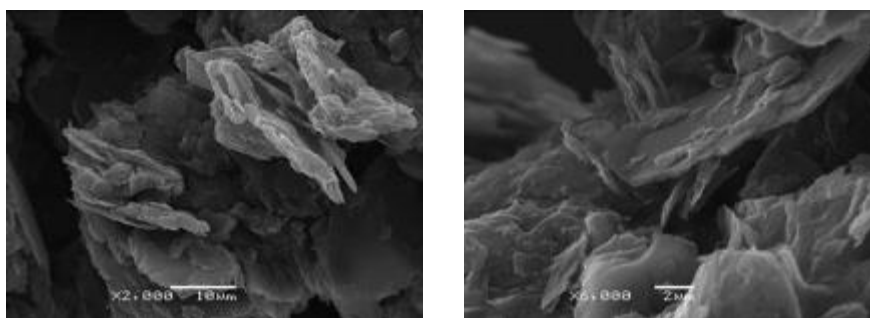


Figure 7.5 SEM micrographs of G-EU-01

The obtained material is heterogeneous and does not appear to be very well exfoliated, as several layers can be distinguished in the figure below and therefore suggesting that the direct exfoliation procedure needs to be optimised. Furthermore, it was possible to spot remaining surfactant, indicating the washing process should be also improved. It is worthy to mention that some individual sheets were identified (Figure 7.6), hence it can be envisaged the prospect of the direct exfoliation as an alternative route to the conventional synthesis from coal liquid-based graphites by the chemical route.

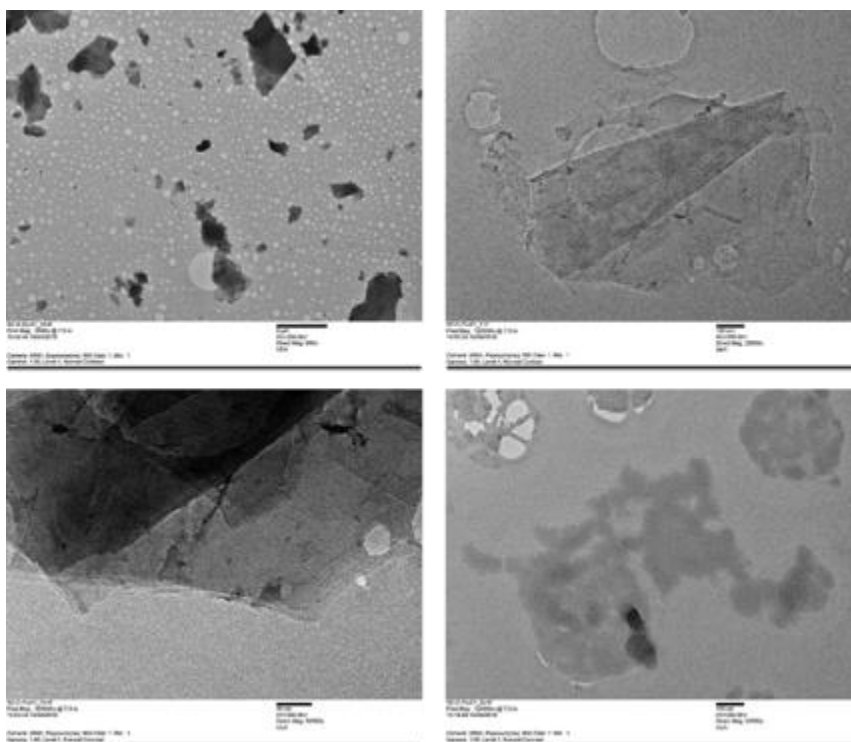


Figure 7.6 TEM images of the sample G-EU-01

Task 7.3 Advanced characterization of the composites AC/Gs

Three composite materials were received to carry out elemental analysis, SEM and nitrogen adsorption. The obtained results and their corresponding discussion have been included in WP5.

Work Package conclusions:

- Exhaustive advanced characterization of the coal-liquid based carbon materials (ACs, Gs and AC/Gs) synthesized during the entire process in terms of morphology, structure, chemical composition and physical properties was carried out.
- The produced ACs (conventional and unconventional) are mainly microporous materials, however those from microwaved precursors present higher surface area and more appropriate properties to be excellent materials for electrodes in supercapacitors.

- Graphene materials from unconventional sources seem to exfoliate better than materials synthesized from AO derived precursors by conventional methods, where accordion-like structures were predominant.
- Thermally reduced graphene oxides synthesized from microwaved raw materials present lower oxygen content, slightly enhanced surface area as well as better accomplishment of Csp^2 content on their surfaces, especially those reduced at 1000 °C.
- Microwave technology can be an alternative way for the synthesis of carbon materials for energy storage with comparable, or even improved, characteristics to those obtained by conventional approaches.

CONCLUSIONS

- Coal derivatives (i.e., free QI-coal tar and anthracene oil) have been shown adequate feedstocks for the preparation of carbon precursors (i.e., pitches) able to be subsequently transformed into carbon materials (activated carbons, graphene and graphene based composites).
- A new technology, based on microwave heating, has been optimized for the preparation of pitches and cokes. This technology is lower time and electric energy consumption than conventional technologies.
- An alternative route to the Hummers method, using supercritical fluids, has been developed for the synthesis of graphene materials.
- Supercapacitors and hybrid systems with improved electrochemical performance have been prepared from coal liquid based materials (activated carbons, graphene and composites).

EXPLOITATION AND IMPACT OF THE RESEARCH RESULTS

Some innovative aspects emerge from the execution of the present project. These can be summarized as follows:

Preparation of pitch, coke and graphite from coal-derived liquids

The preparation of pitches from coal-derived liquids, and subsequently cokes and graphites, has been directly carried out from tar and its heaviest distillation fraction (i.e., anthracene oil) by oxidative thermal condensation.

The direct use of tar requires the elimination of its major impurities, i.e. solid particles in suspension and metallic impurities. This process has been performed by means of a specific continuous process. This process can be perfectly scalable from a technical and economical point of view. This is because it requires mild operation conditions and the reagents used can be recirculated after distillation. However, and by simple mass balance, the preparation of a clean fraction involves the formation of a fraction in which impurities are concentrated. Therefore, the industrial implementation of the results requires a technical and commercial effort to search a scope for using the waste fraction.

The route based on the oxidative thermal condensation of anthracene oil offers an alternative route, technically and economically, equal or even more attractive than the use of tar. The industrial implementation for producing anthracene oil pitches is ready to be carried out once two previous premises are fulfilled:

- The process requires an additional technological innovation. The process use air as a reagent (mixture of oxygen and nitrogen) and nitrogen generates a current of inert gas in the process that drags volatile organic compounds, generating some vents of very difficult post-treatment to avoid a negative environmental impact. The level of investment required for the treatment of these vents seriously penalizes the economy of the process. In this regard, IQNSA is currently carrying out a technological implementation of the process through the use of pure oxygen as reactive. The process needs to be readjusted as it substantially changes the reactivity of the components, and requires the evaluation and conditioning of the safety measures of the industrial plant.
- The industrial implementation of these results requires finding a potential market for these products of at least 15 ktons/year. The pitches synthesized by this process could not only be valid for the manufacture of the materials under study in this project, but also for all those uses where the presence of primary QI particles is not required. However, a market that shows a sufficient added value and has a volume that justifies the investment has still not been found.

It is worth highlighting the flexibility of the anthracene oil pitches process to produce precursors of different crystallographic structure, maintaining the structural perfection of graphite. Different crystallographic structures subsequently provide different properties that have been evaluated throughout the project; characteristics especially sensitive for the preparation of the subsequent graphene.

Preparation of graphene by direct exfoliation of coal-liquid based graphite by using supercritical fluids

During the execution of this project, two novel processes have been developed for the production of graphene materials: mechanical exfoliation and use of hydrogen peroxide under supercritical conditions. These processes can be considered sustainable (they do not generate toxic wastes), scalable (they can be produced under continuous regimen and close to a capacity what could be appropriate for production at an industrial level) and economic (they involved low energy costs).

The way for obtaining graphene via oxidation route with hydrogen peroxide under supercritical water conditions also offers the possibility of obtaining graphene oxide (a product also useful for different applications) with the peculiarity of being able to be thermally reduced by hydrothermal reduction in situ, only by coupling an intermediate reservoir between the reactor and the expansion tower. The process also offers the possibility of producing exfoliated materials directly from coke avoiding a previous stage of graphitization, thus reducing operating costs. However, the process requires to be optimized because the heterogeneity of the resultant materials, especially when graphite is used as raw material. Although this process does not offer the quality of graphene produced by the Hummers method, it can be used in various applications that currently have a high relative consumption.

Regarding the materials that have been obtained through oxidative exfoliation under supercritical water regime, the most important ones are the Graphene Quantum Dots (GQDs). It is important to remark that, when compared to those currently offered in the market, those produced by this procedure maintain their fluorescence over time. Nevertheless, the process requires to be optimized in order to enhance their fluorescence intensity.

Design of a Microwave Heating Laboratory and Pilot Equipment for the preparation of carbon precursors and activated carbons

Using a special designed microwave heating pilot equipment, anthracene oil-based isotropic/mesophase pitches with a desired softening point were produced. Anthracene oil microwave polymerization revealed:

- Microwave heating is a feasible alternative for all the polymerization stages (oxidation, thermal treatment, residence time) with an accurate temperature control.
- Conversions between 30 and 40 wt.% for mesophase pitches can be obtained for 4 kg of anthracene oil load and 5 h of total treatment, with only an energy consumption of 3 kW.

This innovative technology was also applied to the production of cokes from pitches. The use of microwave power supposes the use of heating rates higher (4 to 10 times) than those used by conventional electric heating, achieving conversion degrees of 45 and 70 wt.%.

These results provide the possibility of scaling the processes, as well as the microwave devices, for obtaining isotropic/mesophase pitches and cokes with improved yields and lower energy consumption than in the case of classical processes.

Microwave technology was also used for producing chemical activated carbons. The results reveal:

- High conversion yield (between 80 and 90 wt.%).
- Excellent microwave response to the reaction materials.
- Production of activated carbons with high specific surface area (between 2200 and 2800 m²/g).

The most important challenge for microwave activation is related to the resistance of synthesis vessels to chemical activating agents under high temperature conditions. Once this limitation is overcome, scaling up could be easily accomplished.

On the basis of all these studies it can be stated that a pilot plant with a production of 1 metric ton per batch can be developed for producing niche products with significant added value.

Additionally to these innovative aspects, the development of the present project has given rise to results with an important scientific and technological interest. These results have been published and disseminated in several journals, conferences and other scientific outputs.

Articles in SCI journals

- 1) E. Miniach, A. Śliwak, A. Moyseowicz, L. Fernandez-Garcia, Z. Gonzalez, M. Granda, R. Menendez, G. Gryglewicz: "MnO₂/thermally reduced graphene oxide composites for high-voltage asymmetric supercapacitors". *Electrochimica Acta* 240, 53-62 (2017).
- 2) A. Moyseowicz, Z. Gonzalez, R. Menendez and G. Gryglewicz: "Three-dimensional poly(aniline-co-pyrrole)/thermally reduced graphene oxide composite as a binder-free electrode for high-performance supercapacitor". *Composites Part B* 145, 232-239 (2018).
- 3) G. Predeanu, S.M. Axinte, M.F. Drăgoescu, Z. González, P. Álvarez, M. Granda, R. Menendez, A. Fiti, B. Acevedo, S. Melendi-Espina, G. Gryglewicz, J.J. Fernández, V. Slăvescu: "Microwave heating as a novel route for obtaining carbon precursors from anthracene oil". *Fuel Processing Technology* (sent).

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- 1) Z. González, G. Predeanu, S. Axinte, J.J. Fernández, I. Călinescu, P. Chipurici, V. Slăvescu, M.F. Drăgoescu, B. Acevedo, S. Melendi-Espina, G. Gryglewicz, R. Menéndez: "Carbon materials from conventional/unconventional technologies for electrochemical energy storage devices". World Conference on Carbon 2017, Abstracts Book, Melbourne (Australia). Oral communication.
- 2) G. Predeanu, S. Axinte, M.F. Drăgoescu, J.J. Fernández, A. Fiti, Z. González, R. Menéndez, V. Slăvescu, A.T. Abagiu: "Mesophase development in an anthracene oil-based pitch by pyrolysis in a microwave field". ICCP Program & Abstract Book. 69th Annual Meeting of the International Committee for Coal and Organic Petrology, September 3-9. 2017, Bucharest, Romania. Schriftenreihe der Deutschen Gesellschaft für Geowissenschaften Heft 92, 125-126. ISBN 978-3-510-49239-8.
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- 4) R. Menéndez, Z. González, G. Predeanu, S. Axinte, J.J. Fernández, I. Calinescu, V. Slăvescu, M. Drăgoescu, B. Acevedo, S. Melendi-Espina, G. Gryglewicz: "Tecnología microondas como alternativa para la obtención de materiales de carbono eficaces en almacenamiento de energía". XIV Congreso Internacional de energía y Recursos Minerales 2018, Sevilla (Spain), 10-13 Abril 2018, p. 373. Oral communication.
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Patents

- 1) A. Fiti, M.F. Drăgoescu, G. Predeanu, S. Axinte, V. Slăvescu, A.T. Abagiu. Procedure for obtaining isotropic pitch by oxidative polymerization of anthracene oil using microwave heating. Patent request (A/00191/19.03.2018) State Office for Inventions and Trademarks (OSIM, in Romania).

PhD Thesis

- 1) PhD: A. Moyseowicz, Kompozyty polimerów przewodzących i nanostrukturalnych materiałów węglowych jako elektroda superkondensatora (Conducting polymers/nanostructured carbon material composites as electrode materials for supercapacitors), Politechnika Wrocławska, Wrocław 2019.

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LIST OF ACRONYMS AND ABBREVIATIONS

AC	Activated carbon
AC/G	Composite material activated carbon / graphene
AI	- Anthracene oil insolubles
AO	Anthracene oil
BE	Binding energy
BET-	Brunauer-Elmet-Teller method
C	Capacitance
C _s	Specific capacitance
CF	Carbon factor/Fixed carbon
CK-	Coke
CT	Coal Tar
CTRom, CTR	Claudiu TOP Rom SRL
CV	Cyclic voltammetry
EDLC	Electrical double layer capacitor
EOX	Electrochemically oxidized
FTIR	Fourier transformed infrared spectroscopy
G	Graphene
GCD	Galvanostatic charge-discharge
GO-	Graphene oxide
Gr	Graphite
GrO	Graphite oxide
H ₂	- Hydrogen
HNO ₃	Nitric acid
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulfuric acid
HT	Hydrothermal treatment
I _D /I _G	ratio of intensities of the D and G bands of a Raman spectrum
INCAR-CSIC-	Instituto Nacional del Carbón, Agencia estatal consejo superior de investigaciones científicas
IQNSA	Industrial Química del Nalón
K	Degree Kelvin
KOH	Potassium hydroxide
KMnO ₄	Potassium permanganate
L ₀	Average pore size
N-AC	Nitrogen-doped activate carbon
Na ₂ SO ₄	Sodium sulfate
NH ₃	- Ammonia
NHE	Normal hydrogen electrode
NaNO ₃	Sodium nitrate
NS	A mixture of nitric and sulfuric acids
O (wt. %)	Oxygen content (determined by elemental analysis)
OM	Optical microscopy
PT	Pitch
PVDF	- Polyvinylidene fluoride
QSDFT	Quenched-solid density functional theory

QI - primary quinoline insoluble
 PSD Pore size distribution
 RP Reaction product
 RP A Reaction product from oxidative polymerization of AO
 RP B Reaction product from chemical polymerization of AO
 S_{BET} Specific surface area from N_2 adsorption at $-196.1\text{ }^{\circ}\text{C}$
 SCs - Supercapacitors
 SEM Scanning electron microscopy
 SP Softening point
 T Temperature
 TEM Transmission electron microscopy
 TGA Thermogravimetric analysis
 TI Toluene insoluble
 TPD Temperature programmed desorption
 TRGO Thermally reduced graphene oxide
 UPB Universitatea Politehnica din Bucuresti
 U Urea
 VOSO_4 Vanadyl Sulphate
 V_{T} Total volume of pores determined from the adsorption isotherm (N_2 , $-196.1\text{ }^{\circ}\text{C}$)
 V_{micro} , V_{DR} Volume of micropores
 V_{meso} Volume of mesopores
 scan scan rate
 WP Work Package
 XPS X-ray photoelectron spectroscopy
 XRD - X-Ray Diffraction

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Anthracene oil-based pitches were prepared at semi-industrial scale, using two methodologies: air-blowing treatment and microwave heating. Air blowing was revealed as a flexible procedure, allowing the manufacture of carbon precursors with different properties. Microwave technology was optimized to produce carbon precursors with similar properties to those obtained by conventional procedures but involving lower time and energy consumption. These carbon precursors were used for the preparation of activated carbons and graphene materials. Regarding graphene materials, two alternative processes to the Hummers method for the exfoliation of graphite have been developed at a semi-industrial scale, both based on supercritical conditions. Several methods were applied to introduce oxygen and nitrogen functional groups on the surface of activated carbons. Oxidative and heat treatment, with air and ammonia, respectively, allowed materials with enhanced oxygen and nitrogen contents, nearly retaining the porous texture. An enhancement of the specific capacitance was obtained due to the pseudo capacitance effect. High-voltage asymmetric super capacitor was assembled based on the modified activated carbons. Moreover, electrochemical performance of both activated carbons and graphene materials from the microwave technology was proved to be comparable to similar materials from conventional technology, thus representing a step forward in the development of more effective active materials. In addition, the synthesis of composite materials (activated carbon/graphene material) offers the possibility of obtaining novel electrodes taking advantage of the better properties of each one of the components. Furthermore, the design of optimized hybrid devices (capacitor/battery) represents a promising alternative to achieve energy storage devices with improved energy density values.

