

Production of A New Materials from Moroccan Oil Shale



Abourriche A^{1*}, Oumam M², Mansouri S^{2,3}, Mouiya M^{1,3}, Rakcho Y¹, Benhammou A¹, Abouliatim Y¹, Alami J³ and Hannache H^{2,3}

¹Laboratory Materials, Processes, Environment and Quality, National School of Applied Sciences, Morocco

²LIMAT-Thermostructural Materials and Polymers Team, Faculty of Science Ben M'sik, Morocco

³Department of Materials Science and Nanoengineering, University of Mohamed VI Polytechnic, Morocco

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***Corresponding author:** Abourriche A, Laboratory Materials, Processes, Environment and Quality, National School of Applied Sciences, Safi, Morocco, Email: a.abourriche@uca.ma

Abstract

This paper evaluates the possibilities to produce new materials, starting from Moroccan oil shales, for different applications. More specifically, we aim at demonstrating that the organic fraction of the oil shales could be used as precursor of carbon fibers and graphitizable carbon, after appropriate chemical treatments resulting in a "maturation" of this organic phase. ts.

Keywords: Oil shale; Supercritical extraction; Carbon fibres; Graphitizable carbon

Introduction

Morocco, with estimated reserves of 93 billion tons [1], is increasingly looking at oil shales as an alternative energy source. Many studies have concentrated on oil shales located in Timahdit and Tarfaya, because of their high proportion of organic matter [2]. Most of the studies focused either on the yield and the quality of the oils obtained by conventional pyrolysis or on the characterization of these oils by different physical and chemical techniques [3-6]. In addition, oil shales have a certain potential for the production of several synthetic products such as cement, sulfur, ammonia, adsorbent carbons, carbon fibers and other chemicals [7-9]. In this work, we explore the possibility of transforming the oil shales to materials with high added value. More specifically, we aim at demonstrating that the organic fraction of the oil shales could

be used as precursor of low-cost carbon fibers or graphitizable carbon, after appropriate chemical treatments resulting in a "maturation" of this organic phase.

Activated Carbon Fibers from Moroccan Oil Shales

Preparation of the precursor of carbon fibers (pitches)

The oil shale used in this work was from the Tarfaya deposit located in the South of Morocco. This deposit consists of several layers that are subdivided in sub-layers, each having a different amount of organic matter. The samples were obtained from the so-called R₃ sub-layer characterized by its high content of organic matter [10-12]. Its chemical composition is given in (Table 1).

Table 1: Chemical composition of the R₃ sub-layer [12].

Composition	Carbonates	Kerogen	Silicates	Pyrite	Bitumen	Metals traces
(wt %)	70	20	7.1	1	0.9	1

Preparation of the raw material

The carbonate-free oil shale was obtained by dissolution of carbonates with HCl [13,14]. The powdered R3 shale (20 g, grain size 0.063-0.08 mm) and 80 mL of concentrated HCl (7 M) were

introduced in an Erlenmeyer. The mixture was then subjected to magnetic stirring for 4 h. The formed CO₂ was trapped by bubbling in a solution of barium hydroxide. After filtration, the solid residue (referred to as RH) was washed carefully with distilled water, dried at 100 °C and stocked in a sealed plastic bag.

Procedures

Supercritical extraction of RH (10 g) with toluene was conducted in a 120 mL stainless steel autoclave equipped with a pressure gauge and heated in a tubular furnace whose temperature, as well as the heating rate, was controlled (Figure 1). The temperature of extraction was 390 °C with a heating rate of 16 °C·min⁻¹ [15]. The maximum pressure reached during this treatment of 120 min was 5.3 MPa and 7.5 MPa for a volume of toluene of 50 mL and 70 mL respectively, beyond the critical point of toluene (320 °C, 4.2 MPa). After being cooled to room temperature, the mixture was extracted in a Soxhlet apparatus

with chloroform for 12 h. The solvent was removed under reduced pressure, and then the organic material was dried for 12 h at 40 °C and weighed. The recovered oil was treated with n-hexane in a 1/10 oil to solvent mass ratio [16]. After stirring for 12 h, the two fractions, soluble (maltenes) and insoluble (asphaltenes), were separated by filtration through Whatman paper, and then dried for 12 h at 40 °C and 80 °C respectively. The maltenes were fractionated in a silica gel column (70-230 mesh, 1 m long and 1.5 cm diameter). Elution of paraffinic, aromatic and polar compounds was performed with hexane, toluene and methanol, respectively [16]. The high-molecular fraction (asphaltenes) constitutes the pitch.

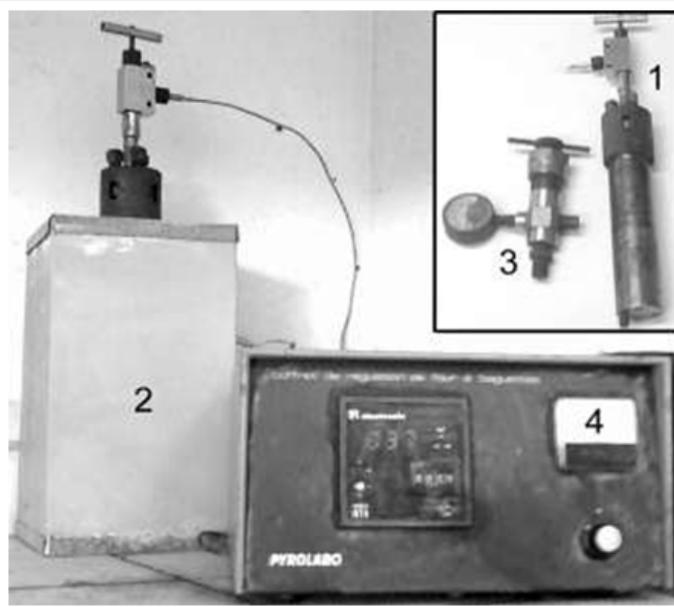


Figure 1: Photograph of the apparatus used for supercritical extraction: (1) reactor; (2) furnace; (3) pressure gauge; (4) regulator.

Preparation of carbon fibers

The black, solid precursor is soluble in toluene and its softening point is about 120 °C. It was melted at 150 °C in a laboratory-made spinning device with a single spinneret, equipped with a filter to remove solid particles from the melt. After extrusion and mechanical stretching, the fiber was thermoset by oxidation in dry air by being slowly heated at atmospheric pressure to the temperature in the range 60-280 °C. The thermoset fibers were pyrolyzed under nitrogen flow. The temperature was progressively raised up to 950 °C with a rate of 5 °C·min⁻¹.

Activation of the carbon fibers

The pyrolyzed carbon fibers were activated with phosphoric acid [17] at different temperatures. The samples were impregnated in H₃PO₄ (10 %) for 1 h and then dried in air at 120 °C for 2 h. The activation reactions were performed in a thermolyne silica electric oven with a temperature control device linked to a thermocouple. The steam generator was placed at the entrance of the reactor. The activation was carried out either under nitrogen or under steam flow. In both cases, the carbon fibers were placed

in the reactor and the temperature was progressively raised at a rate of 5 °C·min⁻¹ up to 500 °C, 700 °C and 850 °C, under nitrogen flow, and then the system was set at the maximum temperature that was maintained for 1 h. The first series (FHN) was treated under nitrogen atmosphere and the second series (FHV) under water vapor (Table 2). At the end of the activation, the oven was cooled to ambient, and then the activated carbon fibers were retrieved and boiled for 2 h in distilled water, then washed, dried and retained for subsequent analyses.

Table 2: Experimental conditions.

Sample	Temp (°C)	Burn off (%)
FHN500	500	4
FHN700	700	12
FHN850	850	19
FHV500	500	10
FHV700	700	18
FHV850	850	24

Characterization of the activated carbon fibers

These activated carbon fibers are essentially microporous. The adsorption isotherm is of type I of the BDDT classification [18] and the t-plot [19], which compares the nitrogen adsorption isotherm obtained for the studied porous solid to a reference

isotherm determined on a nonporous solid, presents a negative deviation from straight line, which is characteristic of micropores. This observation is confirmed by the B hysteresis characteristic of pores, according to the de Boer classification [20]. The surface area and the pore diameter calculated by the BET method [21] are given in (Table 3).

Table 3: Surface area and pore diameter of prepared samples.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	R_p (nm)
FHN500	39	2.3
FHN700	481	1.2
FHN850	542	1.9
FHV500	516	1.8
FHV700	698	2.1
FHV850	846	2.4

Scanning electron microscopy (SEM)

Samples FHN850 and FHV850 were analyzed by SEM. The micrographs in (Figure 2) show little pores at the outer surface of the two activated fibers, but micrographs of cross section surfaces

present a great difference between the samples. They reveal that activation under steam flow produced fibers with a homogeneous repartition of porosity. In the case of activation under nitrogen, the experimental conditions used were insufficient to create a large porosity, which is observed only at the surface of the fiber.

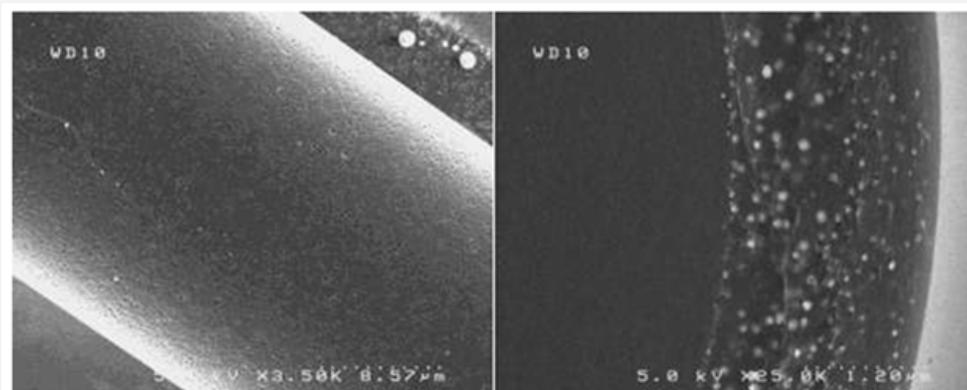


Figure 2: SEM micrographs of the activated carbon fibers FHV (left) and FHN (right).

New Graphitizable Carbon Obtained from Moroccan Oil Shales

Our objective was to study the possibility to produce new pitches by using the insoluble fraction resulting from the separation by hexane of the oils recovered from Moroccan oil shales. The evolution of the degree of graphitization of carbons resulting from the pyrolysis of oil shale pitches in the temperature range 1100-2800 °C was studied by Raman spectroscopy in order to determine the operating conditions that were likely to give a pitch leading to a graphitizable carbon [22,23]. The pitches obtained under different conditions of treatment by supercritical extraction were

subjected to pyrolysis at 1100 °C and subsequent heat treatments between 1400 and 2800 °C, in order to obtain carbon materials with different degrees of graphitization. After each treatment, the residue was characterized by Raman spectroscopy (Figure 3). The results obtained show that the degree of graphitization was strongly dependent on the composition of the pitch. Interestingly, it was found that the organization of carbon began at relatively low temperatures. Thus, beyond 1400 °C, a marked structural evolution occurred, leading to a more or less ordered material, according to the composition of the pitch and its preparation conditions. Moreover, phenol is a good extraction solvent under the operating conditions used, leading to carbon pitches with a

high graphitization aptitude. The pitches treated at 2800 °C were also analyzed by SEM (Figure 4). These images largely confirm the results of analysis by Raman. Indeed, the pitches treated at 2800°C have a rather unique structure and surprising. This structure is

similar to a laminated structure with the appearance of regular hexagons, which is characteristic of a good carbon structural organization.

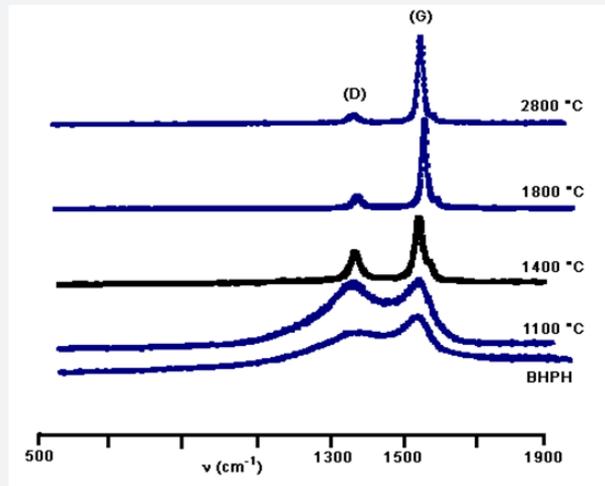


Figure 3: Raman spectra of pitch treated at different temperatures.

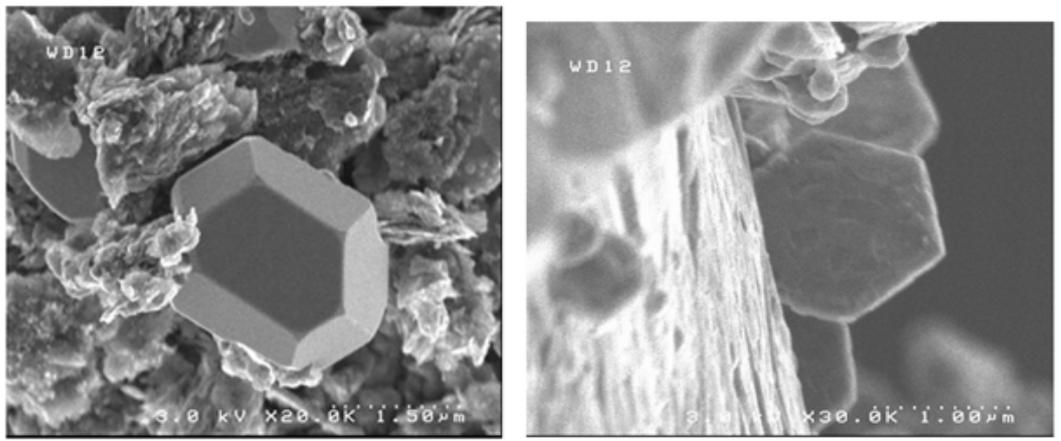


Figure 4: SEM photographs of the pitches treated at 2800 °C.

Conclusion

The present work is part of a more general program for the exploitation of natural resources, and more particularly the Moroccan oil shale deposit of Tarfaya. We have presented a new process using supercritical extraction to produce activated carbon fibers or graphitizable carbon. The fibers exhibit low mechanical properties owing to the isotropic character of the precursor and the absence of mechanical stretching during pyrolysis. The activation of the fibers with phosphoric acid at 850 °C yields a carbon fiber with a specific area of 800 m²·g⁻¹. These fibers can be used as adsorbent or filter in environmental applications.

We also prepared new pitches starting from the extraction of Moroccan oil shales. Aptitude for graphitization of carbon resulting from their pyrolysis at increasing temperatures was studied by Raman spectrometry. The degree of graphitization was strongly dependent on the composition of the pitch. Interestingly, it was found that the organization of carbon began at relatively low temperatures. Thus, beyond 1400 °C, a marked structural evolution occurred, leading to a more or less ordered material, according to the composition of the pitch and its preparation conditions.

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