



A novel approach for the production of chemically activated carbon fibers



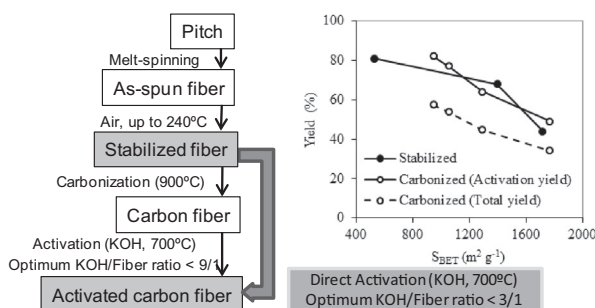
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HIGHLIGHTS

- Chemically activated carbon fibers can be obtained directly from stabilized fibers.
- The use of stabilized fibers saves up to a 70% of activating agent.
- Activated fibers from stabilized and carbonized fibers exhibit similar porous texture.
- The overall yield of the activation process is increased with stabilized fibers.

GRAPHICAL ABSTRACT



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ABSTRACT

The direct chemical activation of pitch-based stabilized carbon fibers (uncarbonized) with a conventional activating agent (KOH) has been studied for the first time. Unlike the traditional activation method, this shorter route merges the carbonization and activation steps into one simple thermal treatment. It also requires up to a 70% less activating agent for a given porous structure, which can reach values of $S_{BET} > 1700 m^2 g^{-1}$. In addition, the overall yield of the activation process is increased. The advantages obtained open up the way to a novel environmentally friendly industrial method of preparing activated carbon fibers.

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1. Introduction

Activated carbons (ACs) have been extremely successful as a remediation solution for air and water purification [1], catalysis [2,3] or energy storage [4], because of their high surface area and adsorption capacity. Furthermore, increasing worldwide environmental concern is also driving the demand for these materials which, according to recent reports, is expected to grow at the compounded annual growth rate (CAGR) of more than 13% by 2017 [5].

Activated carbon fibers (ACF) show similar properties to ACs but having a fibrillar shape. Compared to granular or powdered activated carbons, they have a higher adsorption-desorption kinetics and lower resistance to bulk flows, their higher manufacturing cost being their main disadvantage [6–8]. Therefore, any new strategy that will reduce the operation cost of the production process will be an opportunity for manufacturers.

Nowadays, ACFs are prepared by the chemical or physical activation of carbon fibers. Compared to physical activation, chemical activation with alkaline hydroxides, such as KOH, provides higher yields and less surface damage during the activation of fiber [9] and so will be the main focus of this study. The overall preparation process (starting from the raw pitch) consists of four consecutive steps: (i) spinning of the parent material (mainly PAN or pitch), (ii) stabilization of the as spun fibers to make them infusible, (iii)

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carbonization of the stabilized fibers up to 900–1000 °C in order to consolidate their carbonaceous structure and (iv) chemical activation (mainly with KOH) of the obtained carbon fibers at temperatures of 700–900 °C, conditions which determine, to a large extent, the textural properties of the activated material [10]. Quiao et al. described the direct activation of stabilized pitch in powder form [11]. Direct physical activation of pitch-based fibers was also reported by Tekinalp et al. [12]. However, to the best of our knowledge, chemical activation of stabilized fibers has not been reported before. The aim of this work is therefore the direct activation of stabilized (non-carbonized) fibers, since the activation process and the carbonization processes occur at relatively similar temperatures. This will result in an overall three step process with a substantial reduction in energy (and time) requirements related mainly with the elimination of previously required carbonization process.

Other factors will also determine the viability of the overall process, the most important being the oxygen at the surface of the fiber. It is well known that in a common activation process, a greater presence of oxygen or a lower carbonization degree lead to higher porous structures after activation [13,14]. This point in particular will be studied in this work.

We report herein the direct chemical activation of stabilized (non-carbonized) fibers, as a function of the activating agent ratio (KOH). The carbon fibers precursor used is a commercial anthracene oil-based pitch. For comparative purposes, stabilized fibers were carbonized up to 900 °C and then activated. This study included a careful analysis of the initial oxygen content of the carbon fibers as well as a detailed characterization of the textural properties of the fibers obtained under different activation conditions. The final yield of the process was also determined. The aim of this study was not only to demonstrate the validity of the shorter process proposed but also to determine its ability to minimize the amount of activating agent required to prepare ACFs with specific textural properties.

2. Materials and methods

2.1. Preparation of stabilized and carbonized fibers

An isotropic anthracene oil-based pitch supplied by NalonChem S.A. (Mettler SP: 248 °C) was used as carbon fiber precursor. This pitch was melt-spun into filaments using a laboratory-scale device (see [Supplementary material](#) for details) [15]. 30 g of pitch was heated up to 285 °C and extruded through a monohole spinneret ($D = 500 \mu\text{m}$) by applying a nitrogen pressure of 1 bar. The as-spun fibers were collected on a spool operating at a winding speed of 250 cm s^{-1} . The fibers were then stabilized at up to 260 °C under an air flow of 333 ml min^{-1} at a heating rate of 1 °C min^{-1} with stabilization isotherms of 1 h at 160, 180, 200, 220, 240 and 260 °C. Some fibers were also carbonized at 900 °C at a heating rate of 2 °C min^{-1} under a nitrogen flow of 400 ml min^{-1} . The soaking time at the highest temperature was 30 min. Both the stabilized and carbonized fibers were cut down to lengths of 1 cm to facilitate their handling.

2.2. Preparation of stabilized and carbonized activated carbon fibers

The stabilized fibers or carbon fibers were placed in a horizontal furnace after impregnation with KOH (KOH/fiber (wt/wt) ratios ranging from 1/1 to 9/1). After they had been purged for 30 min, the mixtures were heated under nitrogen flow (400 ml min^{-1}) at 5 °C min^{-1} . The activation temperature used was 700 °C and the holding time was 1 h. After activation, the samples were washed repeatedly with 3 M HCl and distilled water until $\text{pH} \sim 7$. The

cleaned samples were dried in an oven at 110 °C overnight. The weight of the dried samples was measured in order to calculate each activation yield. The activated samples were labeled as A-B/C, where A is the carbonization degree of the fiber before activation (S: stabilized fiber, C: carbon fiber) and B/C is the KOH/fiber (wt/wt) ratio.

2.3. Characterization of ACF

The elemental analyses of the parent pitch and the stabilized and carbonized fibers were performed by means of a LECO-CHNS-932 micro-analyzer and a LECO-VTF-900 furnace coupled to the microanalyzer. The morphology of the fibers after activation was examined by scanning electron microscopy (SEM) using an Evo LS15 Zeiss microscope. The textural parameters of the activated fibers were determined from the N_2 adsorption-desorption isotherms at 77 K (Nova 2200, Quantachrome). The samples were previously outgassed overnight at 300 °C before adsorption/desorption analyses. The specific surface area (S_{BET}) was calculated using the BET method. The amount of nitrogen adsorbed at a relative pressure of $p/p_0 = 0.96$ was used to determine the total pore volume (V_p). The micropore volume (V_{DR}) was estimated by applying the Dubinin-Radushkevitch equation. The mesopore volume (V_{me}) was calculated as the difference between total pore volume and micropore volume. Pore size distributions (QSDFT) were also calculated from the isotherm data.

3. Results and discussions

Following standard industrial procedures to produce isotropic carbon fibers from pitch, a commercially available anthracene oil-based pitch was first melt-spun into green fibers (see [Supplementary material](#) for details) and then stabilized with air to produce the stabilized fibers, according to [Fig. 1](#).

During stabilization, the total oxygen content in the stabilized fibers (S), as determined by elemental analysis, increased from 2.3 wt% in the as-spun fibers to 8.3 wt%. The average diameter of the as-spun fibers ($27.0 \pm 4.0 \mu\text{m}$) also increased to $31.5 \pm 3.5 \mu\text{m}$ due to oxygen functionalization. In the industrial procedures, the oxygen that is introduced prevents the green fibers from melting during the subsequent carbonization step (process which eliminates the oxygen functional groups), when the carbon fibers are produced. The carbonization of the stabilized fibers up to 900 °C produces isotropic fibers (see [Supplementary material](#) for details) with negligible oxygen content (as determined by elemental analysis) and consequently reduces the fiber diameter to $22.0 \pm 4.0 \mu\text{m}$. A detailed analysis of the oxygen containing functional groups at the surface of the stabilized fibers was performed by XPS analysis

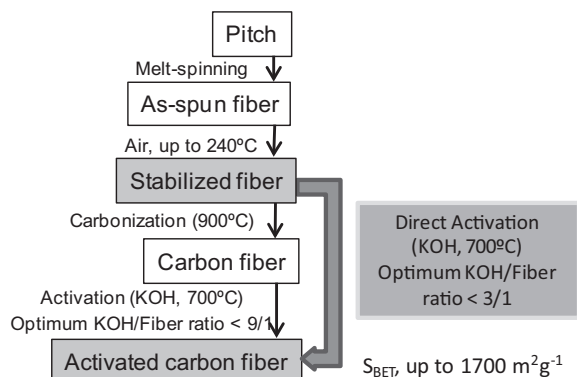


Fig. 1. Scheme of the activation of stabilized and carbonized fibers.

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