

# A novel approach for the production of chemically activated carbon fibers

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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  $S_{\text{BET}} > 1700 \text{ m}^2 \text{ g}^{-1}$ . 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.

## **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 [6,7,8]. Therefore, any new strategy that will reduce the operation cost of the production process will be an opportunity for manufacturers.

Nowadays, ACF 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) consist 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) carbonization of the stabilized fibers up to 900-1000°C in order to consolidate their carbonaceous structure and iv) the 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 fiber 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  $250 \text{ cm s}^{-1}$ . The fibers were then stabilized at 260 °C under an air flow of  $333 \text{ ml min}^{-1}$  at a heating rate of  $1 \text{ }^\circ\text{C min}^{-1}$  with stabilization isotherms of 1h at 160, 180, 200, 220, 240 and 260 °C. Some fibers were also carbonized at 900 °C at a heating rate of  $2 \text{ }^\circ\text{C min}^{-1}$  under a nitrogen flow of  $400 \text{ ml min}^{-1}$ . 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 ( $400 \text{ ml min}^{-1}$ ) at  $5 \text{ }^\circ\text{C min}^{-1}$ . The activation temperature used was  $700^\circ\text{C}$  and the holding time was 1 hour. 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  $110 \text{ }^\circ\text{C}$  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 analysis of the parent pitch and the stabilized and carbonized fibers was 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  $\text{N}_2$  adsorption-desorption isotherms at 77 K (Nova 2200, Quantachrome). The samples were previously outgassed overnight at  $300 \text{ }^\circ\text{C}$  before adsorption/desorption analyses. The specific surface area ( $S_{\text{BET}}$ ) 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 ( $V_{\text{P}}$ ). The micropore volume ( $V_{\text{DR}}$ ) was estimated by applying the Dubinin-Radushkevitch equation. The mesopore volume ( $V_{\text{me}}$ ) 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 Figure 1.

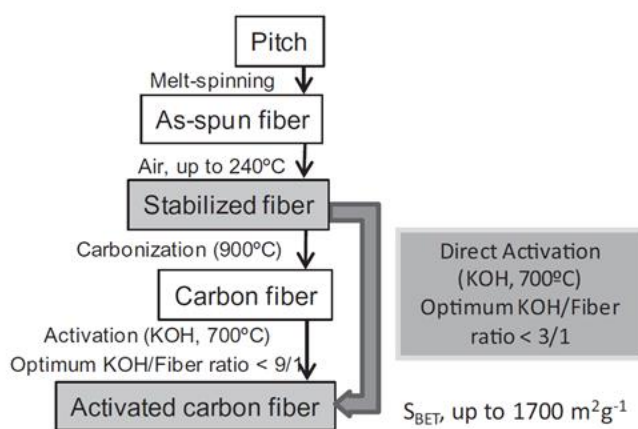


Fig. 1. Scheme of the activation of stabilized and carbonized fibers.

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  $900^\circ\text{C}$  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 (Figure 2a). It can be observed that the amounts of OC=O and C=O groups are similar (1.9%) and slightly lower than the amount of C-O groups (2.9%). FTIR analysis (Figure 2 b) also corroborated the formation of cross-linked structures, in the form of C-O-C bonds ( $1700 \text{ cm}^{-1}$ ) and anhydrides of carboxylic acids (shoulders at  $1760$  and  $1832 \text{ cm}^{-1}$ ). These oxygen groups and cross-linked structures prevent stabilized fibers from melting during subsequent carbonization. This suggests that direct activation with KOH of stabilized fibers can be also a suitable procedure to obtain ACF maintaining their fibrillar shape.

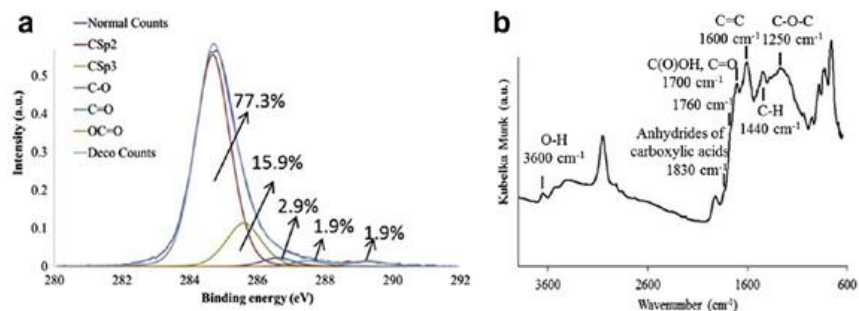


Fig. 2. XPS C1s curves and deconvolution (a) and FTIR spectrum (b) of stabilized fibers.

The as prepared stabilized and carbonized fibers were then used to produce the activated carbon fibers by chemical activation with KOH (KOH/fiber ratios of 1/1 to 9/1). The activation temperature selected was  $700^\circ\text{C}$ .

SEM analysis of all the activated fibers (Figure 3) showed that for both stabilized (S-1/1, S-2/1 and S-3/1) and carbonized (C-3/1, C-5/1, C-7/1 and C-9/1) fibers, the fibrillar shape is preserved in the resulting activated carbon fibers. However, it was also observed that in the case of

stabilized fibers the use of a KOH/fiber ratio higher than 3/1 yields a material in which the fibrillar shape exhibit a highly developed porosity, while in the case of the carbonized materials this ratio can be increased up to 9/1 before a similar porosity development is observed. Also, the presence of large macropores is more marked in the case of the direct activation of the stabilized fibers.

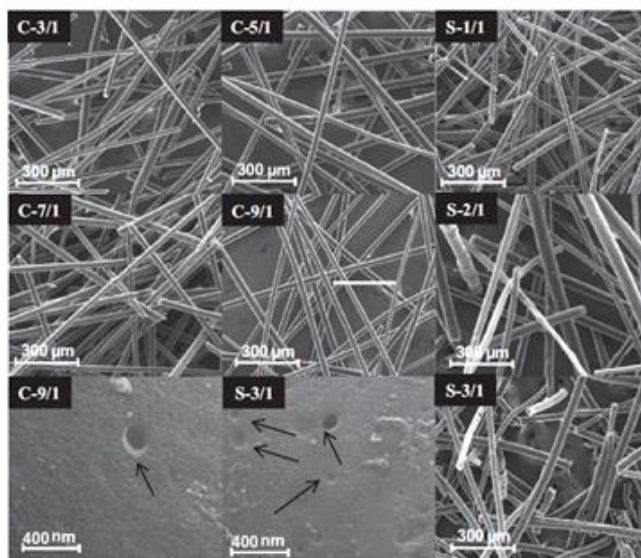


Fig. 3. SEM images of carbon fibers activated with KOH from stabilized fibers (S-X) and carbonized fibers (C-X).

$N_2$  adsorption isotherm analysis of the fibers (Figure 4, a-b) confirmed the success of the activation process for both the carbonized and stabilized samples. Furthermore, all the isotherms are of Type I, which is characteristic of highly microporous materials: There is a sharp knee that becomes wider when higher proportions of KOH are used (broadening of the pore size distributions). There are however, differences between stabilized and carbonized activated fibers. The most relevant is that the stabilized fibers exhibit hysteresis loops indicating the formation of mesopores.[16] These data are confirmed by the corresponding QSDFT pore size distributions of these samples (Figure 4, c-d). All samples exhibit a narrow micropore size distribution centered



at  $\sim 7 \text{ \AA}$ , but only the three stabilized samples and C-9/1 show other relative maximums at higher pore sizes (narrow mesopores,  $< 30 \text{ \AA}$ ), possibly due to the collapse of the micropore walls.

The development of porosity was quantified by applying the Dubinin-Raduskewich equation (see supplementary material for details). As expected, in all the samples the BET surface area increases with the KOH/fiber ratio for both types of fibers (Figure 5a). The most activated carbonized sample, C-9/1, reaches a maximum  $S_{\text{BET}}$  value of  $1770 \text{ m}^2 \text{ g}^{-1}$ . This value is similar to that obtained for the most activated sample, S-3/1, which reaches a  $S_{\text{BET}}$  of  $1720 \text{ m}^2 \text{ g}^{-1}$ . This lower consumption (and therefore of handling) of activating agent also exhibit certain environmental benefits of this novel activation route.

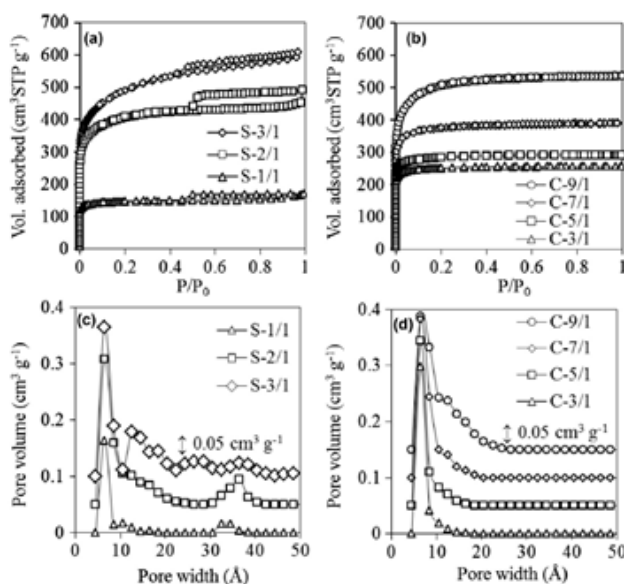


Fig. 4.  $\text{N}_2$  adsorption isotherms (a, b) and QSDFT pore size distribution (c, d) of stabilized fibers (a, c) and carbonized (b, d) activated with KOH.

From an analysis of the variation in microporosity formed as a function of the activating agent used (Figure 5b) it can be concluded that, at lower KOH/fiber ratios, both types of fibers exhibit a similar trend with the preponderant formation of micropores. It seems therefore that, although there is a higher amount of oxygen containing functional groups in stabilized fibers, this has not

a significant impact on the micropore formation during the process. It can be observed, however, that at the highest KOH/Stabilized fiber ratios there is a substantial increase in mesopore formation. The increase in mesopore formation (Table 1) can be assigned to the high reactivity of the stabilized fibers at higher concentrations of KOH, resulting in the collapse of the microporous network and the consequent formation of mesopores and macropores. This behavior, which has also been observed in the case of other activated carbon fibers when high amounts of activating agent are used [4], indicates that the control of the textural properties of the activated stabilized fibers requires a careful control of the concentration of the activating agent used.

Although the exact mechanism of the alkali mediated activation process of carbons is not well understood, it is generally accepted that the process is mainly governed by the overall reaction stoichiometry between KOH and carbon (eq 1) [17]:



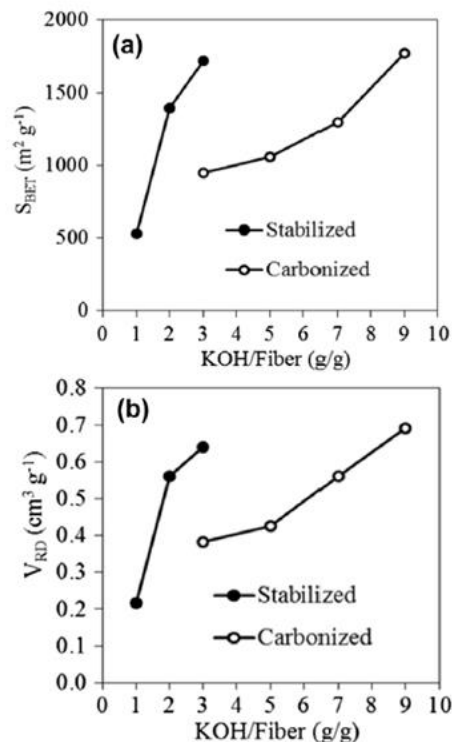


Fig. 5. BET surface area vs. KOH/fiber ratio (a) and micropore volume vs. KOH/fiber ratio (b) of activated fibers from stabilized and carbonized fibers.

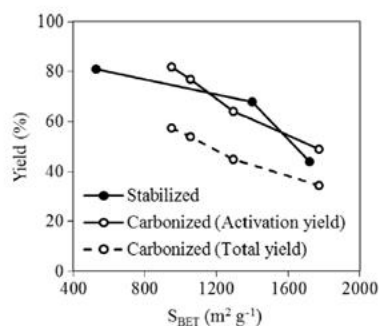
Since the infusibility of the fiber (which is related to the presence of C-O functional groups – mainly cross-linking moieties- etc.) is maintained to some extent in the stabilized fibers during activation, it seems that the reactivity with KOH does not destroy the crosslinking system. We therefore propose that the higher reactivity of the stabilized fibers compared to the carbonized ones could be related to a lower reactivity of the carbonized material [18] and/or a higher reactivity of the hydrogen formed during the activation (eq. 1) with the formation of “nascent” sites upon the desorption of the oxygen functional groups resulting in the formation of methane and yielding another active site [19].

**Table 1**  
Activation data of carbonized and stabilized activated carbon fibers.

Sample	Activation yield (%)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{P}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{DR}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{me}}$ ( $\text{cm}^3 \text{g}^{-1}$ )
C-3/I	82 (58) <sup>*</sup>	948	0.40	0.33	0.07
C-5/I	77 (53) <sup>*</sup>	1056	0.45	0.43	0.02
C-7/I	64 (46) <sup>*</sup>	1294	0.60	0.56	0.04
C-9/I	49 (38) <sup>*</sup>	1770	0.83	0.69	0.14
E-1/I	81	527	0.26	0.22	0.05
E-2/I	68	1396	0.76	0.56	0.21
E-3/I	44	1720	0.98	0.64	0.34

<sup>\*</sup> Total activation yield taking into consideration the carbonization yield.

One important point to bear in mind during the activation of fibers is the carbon yield obtained in the activation process. As expected, during the activation of stabilized and carbonized fibers this yield decreases with the increase in the  $S_{\text{BET}}$  (Figure 6, continuous lines), as a consequence of porosity development. The activation yield obtained for a given  $S_{\text{BET}}$  is comparable for stabilized and carbonized fibers. However, it must be taken into account that stabilized fibers were not subjected to carbonization treatment which, in the case of anthracene oil-based fibers, has an inherent yield of  $\sim 70\%$ . The overall yield for the activation of carbon fibers (Figure 6, dotted line) is therefore around 20-30 % less than in the case of the activation of stabilized fibers. This difference diminishes at the highest degree of activation of stabilized fibers, probably as a consequence of the material loss during the collapse of the micropores and formation of mesopores and macropores. This extra 20% yield is therefore another advantage of the unified process compared to the standard methods.



**Fig. 6.** Yield of activation vs.  $S_{\text{BET}}$  obtained for the KOH activation of stabilized and carbonized fibers.

## 4. CONCLUSIONS

Direct activation of stabilized fibers is a suitable route for the preparation of ACF. This methodology unifies the carbonization and the activation in one single thermal treatment, which inherently represent some technical and economic advantages compared with the traditional activation of carbon fibers. The textural properties of the activated carbon fibers obtained by both methodologies leads to highly microporous activated fibers and with BET surface area that can reach values up to  $1700 \text{ m}^2 \text{ g}^{-1}$ . The use of stabilized fibers leads also to additional formation of mesopores. However, the amount of activating agent required to reach those values is much lower in the case of the activation of stabilized fibers, which requires a more careful control of the KOH/fiber ratio used. The advantages of the unified process also include an increase, of around a 20%, in the carbon yield of the overall process.

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**Appendix A: supplementary material.** This information includes a description of the melt-spinning apparatus used and SEM characterization of the fibers produced.

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Table captions:

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Figure captions:

**Figure 1:** Scheme of the activation of stabilized and carbonized fibers

**Figure 2:** XPS C1s curves and deconvolution (a) and FTIR spectrum (b) of stabilized fibers

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**Figure 4.** N<sub>2</sub> adsorption isotherms (a,b) and QSDFT pore size distribution (c,d) of stabilized fibers (a,c) and carbonized (b, d) activated with KOH.

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