



Effect of supercritical fluid activation on the diameter of carbon fibres



Jessica Montero^a, M. Angel de la Casa-Lillo^b, M. Jesús Sánchez-Montero^a,
Nicolás Martín-Sánchez^a, Carmen Izquierdo^a, Francisco Salvador^{a,*}

^a Dpto. Química Física, Facultad de Química, Universidad de Salamanca, Plaza de la Merced s/n, 37008 Salamanca, Spain

^b Instituto de Bioingeniería, Dpto. de Ciencia de Materiales, Óptica y Tecnología Electrónica, Universidad Miguel Hernández, Edificio Vinalopó, Avda. de la Universidad s/n, 03202 Elche, Alicante, Spain

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ABSTRACT

This work is a comparative study of the variations in the structure of a carbon fibre activated with supercritical H₂O and CO₂ vs. steam and CO₂ at atmospheric pressure (conventional process). The appearances of the external and internal surfaces, fibre size, external and internal mass loss, density, porosity, and fragmentation, etc. were measured and analysed. The results are explained by the different reactivity of the supercritical fluids compared with the steam and CO₂ at atmospheric pressure. The results are coherent with a gasification model based on percolation theory, and special emphasis is given to fibre disintegration once the carbonaceous matrix porosity has reached a critical value.

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1. Introduction

Activated carbon fibres (ACFs) are now one of the most promising materials for use as adsorbents, catalytic supports and catalysts owing to their elevated specific surface area and good pore size distribution. ACFs have significant advantages over similar materials, such as activated carbon, because they exhibit higher adsorption rates and capacities, together with a more homogenous porosity [1].

The most common procedure used to prepare these materials is to partially gasify carbonised fibres (CFs) using oxidising gases at high temperatures. The final goal is to maximise pore development and minimise external mass loss in the carbonised fibre. In general, the development of porosity depends on the nature of the char, the oxidising agent employed, and the experimental conditions used during gasification. The initial porosity of the char is important because part of it is consumed during gasification. What remains lead to the development of larger pores, greater surface area, greater volume, etc. In light of this, many studies addressing the preparation of adsorbent carbonaceous materials have focused

on the effects of the nature of the char on porosity. Steam and CO₂ at atmospheric pressure (ATCO₂) are common oxidising gases that activate slowly, allowing their molecules to diffuse into the char structure and generate widespread porosity [2]. Consequently, materials with elevated microporosities are obtained, although the pores are wider when the char is activated with steam.

The preparation of adsorbent carbonaceous materials using supercritical fluids was initially proposed by Salvador et al. [3] Since then, research in this area has been scarce and conflicting results have been reported. Li et al. [4] reported that carbon fibres activated using supercritical fluids have greater mesoporous development than with steam activation. Similar results were reported by Cai et al. [5] for the preparation of activated carbon microspheres from a phenolic resin using supercritical water (SCW) and steam. These authors suggested that the differences in porosity would be because the activating agents use different gasification pathways. Li et al. [6] activated vapour-grown carbon fibres by exposing them to SCW and supercritical CO₂ (SCCO₂) during 10 min. Despite this brief activating time, the low surface area of the original material resulted almost doubled after both treatments, although they found that the pore size was slightly modified in the range of 1–5 nm. Comparative studies carried out on the preparation of activated carbon from carbonised olive pits [7], oak wood and anthracite [8] using SCW and steam have also been described. These studies highlight how the reactivity and gasification mechanisms of SCW differed from those of steam. The special properties and the ability of SCW to penetrate the pore structure of these materials increase the reaction rate and

* Corresponding author. Tel.: +34 923 294478; fax: +34 923 294574.

E-mail addresses: jessicamg@usal.es (J. Montero), mcasa@umh.es (M.A. de la Casa-Lillo), chusan@usal.es (M.J. Sánchez-Montero), nicolas.martin@usal.es (N. Martín-Sánchez), misiego@usal.es (C. Izquierdo), salvador@usal.es (F. Salvador).

have a direct effect on the development of porosity. In two subsequent works [9,10], the authors studied CF activation using SCW and SCCO₂. Again, the ACFs exhibited different textural characteristics with respect to activation with steam and ATCO₂. The increased reactivity of the fibre with supercritical fluids suggested a change in the reaction mechanism when supercritical fluids were used. This has been confirmed recently in a broad gasification study with water under pressures ranging from 1 to 1000 bar [11]. Although the different textural characteristics of the fibres prepared using the four activation agents have been established [9,10], the actual factors that control the development of char porosity must be determined and studied in depth. Any variation undergone by char during activation, such as structural changes (size, fragmentation, appearance of the internal and external surfaces, mass loss, density, porosity, etc.), diffusional limitations, limitations in the chemical reaction, etc., must be considered.

In light of the above, the present work compares the structural variations undergone by a CF during its activation with these four agents. The results provide a common gasification model able to explain the different evolution of the porous structure of the fibre during activation.

2. Materials and methods

2.1. Preparation of ACFs

String-shaped phenolic fibres, Novoloid (supplied by Kynol), were carbonised at 700 °C under an inert N₂ atmosphere. CFs were very rich in carbon (C: 95.5%; N: 0.10%; H: 0.52%; O: 3.88%) and lacked a mineral content (absence of ash). The objective was working under such conditions at which the four activating agents had similar reactivities. Our previous experience revealed that the more reactive agent was SCW and the less reactive one was ATCO₂, and their reactivities increased as the fluids were heated up [9,10]. As a result, CFs were activated with (i) SCW at 670 °C and 29 MPa, (ii) steam at 750 °C and atmospheric pressure, (iii) SCCO₂ at 775 °C and 10.5 MPa, (iv) ATCO₂ at 800 °C. The nomenclature used to refer to the different series of ACFs is as follows: a number indicating the activation temperature, followed by several letters indicating the activation agent (steam: S; CO₂ at atmospheric pressure: ATCO₂; supercritical water: SCW; supercritical CO₂: SCCO₂) and a number indicating the burnoff. A more detailed description of the experimental procedure has been reported in previous studies [9,10].

CF and all the ACFs prepared were characterised texturally from their N₂ adsorption–desorption isotherms at –196 °C by using a Micromeritics ASAP 2010.

2.2. Scanning electron microscopy (SEM) and digital photography

The changes in the external surface and the porosity of the fibres during activation were studied using scanning electron microscopy (SEM) images, which were also used to measure the diameters of the ACFs. For this, string samples were cut to lengths of approximately 5 mm at different times during activation. The samples were always cut from the same end to guarantee homogeneity. A scanning electron microscope, model ZEISS–DMS–942, was used. The diameters of the ACFs and CF were determined by averaging 400 measurements from randomly selected fibres. Fig. 1 shows how these measurements were performed. We took the precaution of measuring just those fibres situated in the planes close to the detector. Those fibres that may be measured through a distorted vision were rejected. The measuring precision of the diameters was estimated as ±0.1 μm, 10 times greater than the measuring precision of the instrument.

Furthermore, the appearance of the prepared ACF strings was analysed via digital photography.

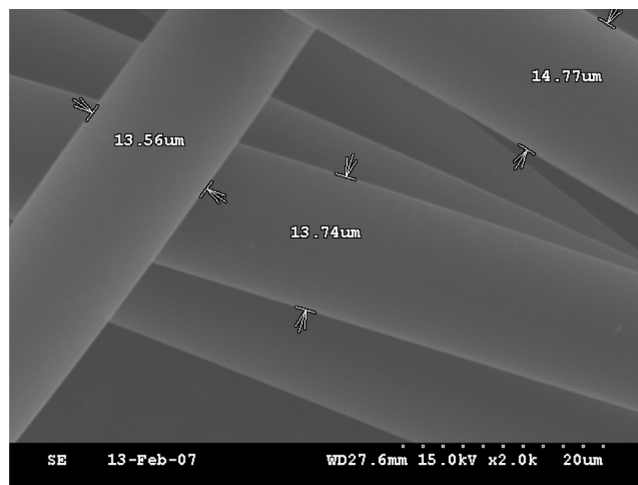


Fig. 1. SEM images for diameter measurements.

3. Results and discussion

3.1. Macroscopic aspects

The first information about gasification of CF with water and CO₂, both supercritical and at atmospheric pressure, can be observed in the digital photographs shown in Fig. 2.

When activation was performed with the two supercritical fluids (Fig. 2b and c), the strings remained unbroken, even at a high burnoff, but their diameters were reduced. This reduction was greater for SCW than for SCCO₂. However, when ATCO₂ was used in the gasification (Fig. 2d), string diameter remained practically constant but the strings exhibited a somewhat deteriorated appearance. They remained unbroken up to an intermediate degree of burnoff, after which they broke up into numerous fragmented ACFs (Fig. 2e). A similar situation occurred when the ACFs were prepared using steam; in this case, the strings underwent a slight degree of thinning, and fragmentation occurred at a higher burnoff (Fig. 2f and g).

These observations indicate that the gasification mechanisms of the four activating agents differ. The supercritical fluids decrease string thickness, while the string undergoes few variations during gasification with the activating agents at atmospheric pressure, despite fragmenting at high burnoffs. Logically, this will affect the textural characteristic and properties of the resulting material.

3.2. Measurements of prepared ACF diameters

The images in Fig. 2 clearly indicate that the fibre diameter changed differently during activation, depending on the activating agent used. To confirm this, the variation in fibre diameter during activation was studied quantitatively. In general, ACFs are materials with well-defined shapes relative to their activated carbon homologues, which make it easier to determine their variation in size during activation. Some authors have measured their dimensions directly via SEM [12–14]. Others have used the total variation in the volume of the bed during gasification [15]. This latter procedure is more appropriate when the starting materials are activated carbons.

In the present study the fibres were considered to be cylindrical and the variation in size was determined by measuring their diameters directly with SEM. The mean diameter was determined by measuring 400 randomly chosen fibres. The plot of these measurements vs. their relative frequency followed a Gaussian distribution. Fig. 3 shows the distribution for the ACFs and CF.

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