

## Preparation and activation of anthracene oil-based fibres

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### Objectives and novelty

General purpose carbon fibres (GPCF) are used as reinforcement in composites and as raw material for the preparation of porous fibres, which find application in separation processes, catalysis or energy storage. The production of GPCF is increasing in order to satisfy their increasing global demand in evolving markets as car manufacturing or civil construction. Although the use of traditional fibres (i.e. PAN-based fibres) is not suitable for these applications because of their high cost and low volume of production, GPCF can be also prepared from binder or impregnating pitches. However, the spinning of these precursors requires several pre-treatments in order to adjust their softening point and to remove the solid particles (i.e. primary quinoline insolubles, QIs) that inhibit fibre formation.

Anthracene oil is a readily available distillation fraction of coal tar (~30 wt.% of coal tar). This fraction constitutes a low cost carbon-rich source that can be easily transformed into a synthetic pitch by oxidative thermal condensation and subsequent thermal treatment. Anthracene oil-based pitches (AOP) are totally free from solid particles and metals, and their softening point can be adjusted during their synthesis, hence making it unnecessary to apply any pre-treatment prior to their spinning. This together with their highly aromatic composition, makes AOP a promising raw material for the preparation of GPCF on an industrial scale.

The main aim of this work is to study the feasibility of AOP as a novel precursor for carbon fibre preparation. The establishment of structure-behaviour relationships during melt-spinning let us optimize the methodology to obtain carbon fibres with the best mechanical performance. This work also includes the design of new routes for the preparation of porous carbon fibres and nitrogen-enriched porous fibres, as well as their assessment in the adsorption of CO<sub>2</sub> and the catalytic oxidation of SO<sub>2</sub>.

### Results

GPCF can be easily prepared by melt-spinning of anthracene oil-based pitches without any pre-treatment at ~ 30 °C above their softening point. The structural characterization of the AOP revealed that pitches with more homogeneous molecular size distribution can be melt-spun with higher yields (up to 35 %) and give rise to fibres with the smallest diameters [1]. After thermal oxidation and carbonization, carbon fibres with diameters of ~15 µm and totally free from defects were obtained (Figure 1). Stabilization time and temperature were found to critically affect both the infusibility of the stabilized fibres and the mechanical properties of the final carbonized fibres. Carbon fibres exhibited high mechanical properties (tensile strength values up to 1100 MPa, Figure 2), which confirms the suitability of anthracene oil-based pitches for carbon fibre preparation [2].

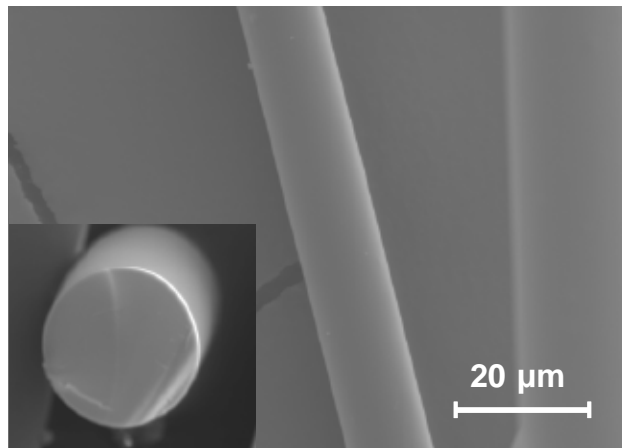


Figure 1. SEM images of carbon fibres.

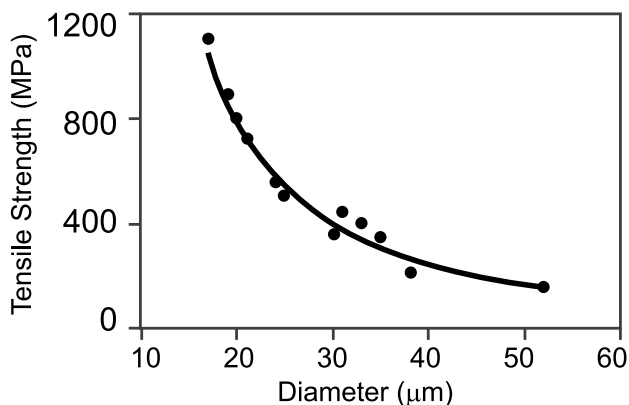
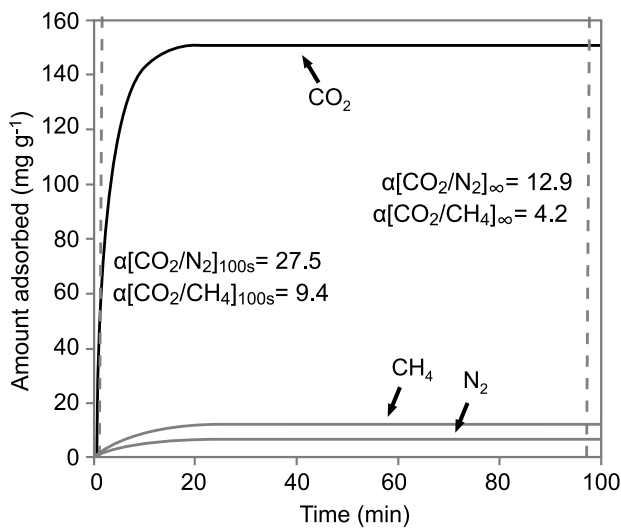


Figure 2. Variation in tensile strength with carbon fibre diameter.

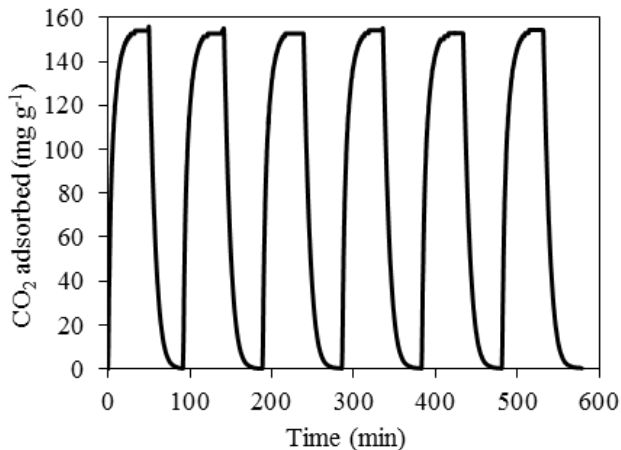
Chemical activation of the carbon fibres led to activated carbon fibres (ACF) with a surface area of 1960 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.89 cm<sup>3</sup> g<sup>-1</sup>. The use of KOH as activating agent and low temperatures (700 °C) gave rise to fibres with narrow pore size distribution, meanwhile the use of NaOH or higher temperatures enlarged the pore sizes up to mesopores range. It was possible to merge carbonization and activation in one single step by direct activation of stabilized fibres, this reducing the amount of activating agent required for ACF preparation to 1/3 [3]. ACF obtained by direct activation of stabilized fibres were tested as electrodes in supercapacitors, showing enhanced activity when compared to fibres obtained by the traditional activation procedure (activation of carbon fibres) [4].

ACF with a nitrogen content up to 7.2 % (mainly in the form of amino groups) were obtained by thermal treatment of ACF with ammonia. Direct ammonization of stabilized fibres allowed carbonization, activation and nitrogen-enrichment of fibres in one single step. These fibres had narrow micropore size distributions and showed very high nitrogen contents (12.3 %) in the form of amine and pyridinic nitrogen. N-enriched fibres were also obtained by mixing the parent pitch with nitrogenized resins (melamine-formaldehyde

resin and urea-formaldehyde resin). The nitrogen content in the activated fibres was ~2 % in the form of quaternary nitrogen and their surface area was 1240 m<sup>2</sup> g<sup>-1</sup>. Due to their high alkalinity and to the high presence of narrow micropores (pore size <7 Å), fibres prepared from pitch and urea-formaldehyde resin showed very high CO<sub>2</sub> capture capacities (3.4 mmol CO<sub>2</sub> g<sup>-1</sup> at ambient temperature). The high alkalinity of these fibres led to very fast kinetics of CO<sub>2</sub> adsorption and, hence, high selectivities towards other molecules as N<sub>2</sub> or CH<sub>4</sub> at short adsorption time (Figure 3). Both the high CO<sub>2</sub> capture capacity and fast kinetics of adsorption and selectivities allow the use of these fibres in swing adsorption devices operating at short time cycles [5]. The fibres could be totally regenerated and maintained their adsorption/desorption kinetics over several cycles (Figure 4).



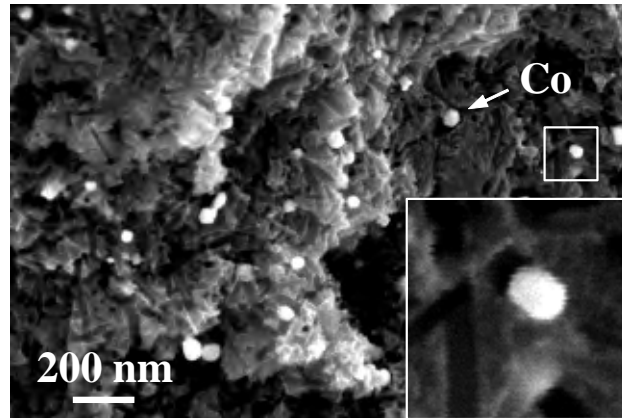
**Figure 3.** Adsorption kinetics of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> and selectivities at 100s and equilibrium.



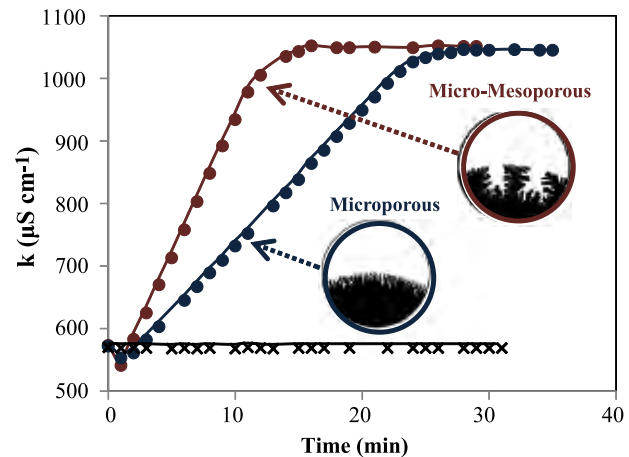
**Figure 4.** CO<sub>2</sub> adsorption-desorption cycles

Micro-mesoporous fibres could be obtained by doping the anthracene oil-based pitch with cobalt naphthenate. After spinning, stabilization and carbonization, fibres contained cobalt nanoparticles with size  $\leq 40$  nm and homogeneous distribution that catalysed the formation of large mesopores (10-50 nm) upon physical activation, maintaining their catalytic activity at very high burn-off values (85 %). The addition of cobalt naphthenate also allowed the use of milder spinning conditions and enhanced spinning yields. Their micro-mesoporous structure, which combines a high surface area with high presence of mesopores, was given by the

combination of two mechanisms: physical activation in absence of metal particles, and catalytic activation in the presence of cobalt nanoparticles, through a channelling mechanism (Figure 5). All the fibres were tested for SO<sub>2</sub> catalytic oxidation in the presence of O<sub>2</sub> and H<sub>2</sub>O by conductivity measurements in liquid media. The catalytic activity was enhanced by the presence of narrow micropores and by nitrogen content. Micro-mesoporous fibres showed, after removal of metal nanoparticles, the highest catalytic activity reported in the literature for microporous and nitrogen enriched fibres (105  $\mu\text{mol min}^{-1} \text{g}^{-1}$ , Figure 6) because of a favoured transport of reactants and products between liquid phase and carbon surface [6].



**Figure 5.** SEM image of Co-containing ACF.



**Figure 6.** Conductivity as a function of time during SO<sub>2</sub> catalytic oxidation.

## Conclusions

Carbon fibres can be successfully prepared by melt-spinning of anthracene oil-based pitches without any pre-treatment. The spinnability of the fibres was determined by the homogeneity of their molecular weight distribution. The final carbon fibres had diameters of 16-22  $\mu\text{m}$  and mechanical properties similar to commercial isotropic carbon fibres.

Activated carbon fibres can be directly prepared by chemical activation of stabilized fibres, and nitrogen enriched activated carbon fibres can be prepared by direct ammonization of stabilized fibres. These new routes of ACF preparation allows to shorten the time, energy and amount of reactants required for their preparation. Doping of pitch with cobalt naphthenate allows the preparation of micro-mesoporous fibres by catalytic activation. These fibres combine high presence of narrow mesopores and large mesopores,

which results in very high catalytic activity towards  $\text{SO}_2$  catalytic oxidation. Nitrogen-enriched activated carbon fibres prepared from mixture of pitch and urea-formaldehyde resin presented high narrow microporosity and high content of quaternary nitrogen in their surface. These fibres showed a high and reversible  $\text{CO}_2$  capture capacity and high selectivities towards  $\text{N}_2$  and  $\text{CH}_4$  at short times.

#### Related publications

[1] Berruero C, Álvarez P, Díez N, Granda M, Menéndez R, Blanco C, Santamaría R, Millan M, Characterisation and feasibility as carbon fibre precursors of isotropic pitches derived from anthracene oil, *Fuel*, 2011; 101, 9-15

[2] Díez N, Álvarez P, Santamaría R, Blanco C, Menéndez R, Granda M, Optimization of the melt-spinning of anthracene oil-based pitch for isotropic carbon fibre preparation, *Fuel Processing Technology*, 2012; 93, 99-104

[3] Díez N, Álvarez P, Granda M, Blanco C, Santamaría R, Menéndez R, A novel approach for the production of chemically activated carbon fibers, *Chemical Engineering Journal*, 2014; In press.

[4] Díez N, Díaz P, Álvarez P, González Z, Granda M, Blanco C, Santamaría R, Menéndez R, Activated carbon fibers prepared directly from stabilized fibers for use as electrodes in supercapacitors, *Materials Letters*, 2014; 136, 214-217.

[5] Díez N, Álvarez P, Granda M, Blanco C, Santamaría R, Menéndez R, N-enriched ACF from coal-based pitch blended with urea-based resin for  $\text{CO}_2$  capture, *Microporous and Mesoporous Materials*, 2014; In press.

[6] Díez N, Alvarez P, Granda M, Blanco C, Gryglewicz G, Wróbel-Iwaniec I, Sliwak A, Machnikowski J, Menendez R, Tailoring Micro-Mesoporosity in activated carbon fibers to enhance  $\text{SO}_2$  catalytic oxidation, *Journal of Colloid and Interface Science*, 2014; 36-40.

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