



Phosphorus functionalization for the rapid preparation of highly nanoporous submicron-diameter carbon fibers by electrospinning of lignin solutions

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This work presents a fast and versatile method to prepare carbon fibers from lignin. It involves the production of submicron-sized phosphorus-functionalized lignin fibers in only one step by electrospinning of lignin/H₃PO₄ solutions. The phosphorus functionalities enable to shorten the conventional stabilization process to avoid fiber fusion from more than 90 h to only 2 h or even to stabilize the lignin fibers in inert atmosphere. The incorporation of H₃PO₄ to the initial lignin solution produces more oxidized spun lignin fibers, due to the reaction of phosphoric acid with the dissolved lignin, generating phosphate (and/or polyphosphate) esters throughout the structure of lignin fibers. These phosphate groups seem to be the responsible for the production of cross-linking reactions during the stabilization step that are, in this case, very active and effective in increasing the glass transition temperature of the lignin fibers, reducing the time needed for the stabilization step and improving this process. Moreover, they promote the chemical activation of lignin fibers and greatly increase their oxidation resistance, avoiding their complete combustion during carbonization under low concentration of O₂ at temperatures as high as 900 °C. The resulting carbon fibers gather different interesting properties, such as sub-micron diameters ($\leq 1 \mu\text{m}$), large surface area ($\approx 2000 \text{ m}^2 \text{ g}^{-1}$), relatively high performance in relation to their mechanical properties for functional applications and a rich variety of uniformly-distributed O and P surface functionalities, which make them very attractive for heterogeneous catalysis, adsorption and electrochemical applications.

Introduction

Porous carbon fibers are relevant materials for many functional applications of industrial and technological interest.¹⁻⁴ Especially, they receive great attention in catalysis, adsorption, gas storage and/or separation processes, electrochemical devices for energy storage and conversion, etc.¹⁻⁴ In spite of such potential applicability, the real and feasible wider utilization of porous CFs demands a reduction of their production costs and/or the development of unique properties or crucial advantages to improve their present competitiveness and performance.^{5,6}

With respect to cost, there is an increased interest and remarkable scientific efforts are currently being focused, even for functional applications, on the replacement of more expensive petroleum-based precursors or different synthetic polymers, and their associated processing, by a cheaper and sustainable manufacture from renewable and low-cost polymeric precursors.^{5,6} The development of carbon fibers with novel and useful properties from lignin has received special attention,⁵⁻¹³ given that it is the second most abundant polymer in nature. In addition, the development of high-value

co-products from lignocellulosic biomass-derived industries, such as biorefineries and pulp and paper mills, could suppose a significant opportunity to minimize their related costs and environmental impacts.^{7,8}

On the other hand, the preparation of carbon fibers by means of a simple and versatile technique, such as electrospinning, entails an advantageous and promising approach.^{14,15} It solves the most important problems associated to conventional melt-extrusion, since it allows the preparation of continuous fibers with considerably smaller diameters (micro- and submicro-scale) at room temperature, directly in a single step. In this sense, we previously presented the preparation of carbon fibers by electrospinning of Alcell[®] lignin without the aid of blending polymeric additives and/or chemical (purification, modification) treatments, thus, considerably reducing the manufacture complexity, time and costs.^{9,10}

After decade-long investigation, however, lignin-based carbon fibers exhibiting competitive performance or unique properties for specific applications are challenging. This usually makes necessary the utilization of additional activation and/or functionalization post-treatments that, apart from slowing down, making complex and raising the costs of the process, may compromise the fibrous structure.¹¹⁻¹³ On the other hand, the production of fibrous carbon materials from lignin is greatly limited by the need of a long oxidative stabilization treatment (more than 3 days), given that lignin shows a glass transition temperature (T_g) far below the temperature

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required for carbonization/activation.^{9,10,16} In this sense, to develop a next-generation of lignin-based carbon fibers, with novel and advanced properties as well as faster production, the design of strategies to control both structural and chemical properties of lignin polymer as well as its thermochemical reactivity will be crucial.

Phosphoric acid has been widely used as chemical agent to prepare activated carbon materials from different precursors, including lignin.¹⁷⁻¹⁹ Thus, the effect of phosphoric acid on the textural properties of the final activated carbon has been widely covered in literature. In particular, the effects of the impregnation ratio and those of the activation temperature and time have been reported in several works.^{18,20} Fierro et al. found that the impregnation of Kraft lignin with H₃PO₄ at H₃PO₄/Lignin weight ratios between 0.7 and 1.7 produces microporous activated carbons and the maximum development of porosity was found at an activation temperature of 550–600 °C. On the other hand, Rosas et al.²⁰ studied the effect of H₃PO₄ on the preparation of carbon fibers from hemp and reported a remarkable development of the mesoporosity without significant damage of the fibers at impregnation ratio higher than 1. The reaction of phosphoric acid with lignocellulosic materials has been also studied.^{20,21} In the case of lignin, phosphoric acid produces de dehydration of the lignin structure and promotes cross-linking reactions to form phosphate and polyphosphate ester-like bonds. In this sense, the incorporation of H₃PO₄ to the lignin solution fibers precursor would favor the cross-linking reactions necessary for stabilization of the fibers, avoiding their fusion during the carbonization process and, at the same time, it would promote the chemical activation upon heating, enhancing the final carbon fibers properties.

In this paper, it is presented a new method to prepare low-cost lignin-based carbon fibers in a remarkably short time. The method involves the electrospinning of lignin/H₃PO₄ solutions into submicro-sized phosphorus-functionalized lignin fibers that can be stabilized at much faster heating rates (up to 60 times), in less than 2 h, and under a wider variety of atmospheres. Furthermore, the method entails the functionalized fibers to undergo a high development of porosity directly during their carbonization at high temperatures by different activation mechanisms acting together. Interestingly, the stabilized phosphorus-lignin fibers, apart from being chemical activated during the carbonization step, can be activated at temperatures as high as 900 °C under a low concentration of O₂, obtaining in this case an extra activation due to the partial gasification of the produced carbonaceous fibers. As a result, the obtained carbon fibers gather a unique combination of textural and chemical properties, i.e. a well-developed microporosity and high surface area (around 2000 m² g⁻¹) in very fine fibers (mainly 400 nm - 1 μm diameter), together with a rich variety of P and O surface functionalities. In addition, the phosphorus-functionalization enhances the oxidation resistance and acidity of these carbon fibers. All these properties have been found very attractive for their potential application in heterogeneous catalysis, adsorption and electrochemistry.

Experimental section

Preparation of electrospun phosphorus-functionalized carbon fibers

Pure lignin fibers were prepared by electrospinning of Alcell® lignin-ethanol solutions.^{9,10} For the H₃PO₄/lignin fibers, spinnable H₃PO₄(85 wt%)/lignin/ethanol solutions (0.3/1/1 weight ratios) were used.²² Solutions were heated at 60 °C and shaken at 200 rpm during 12 h, obtaining a viscosity (350 – 450 cPs) suitable for electrospinning. The lignin solution flow rate was 3 cm³ h⁻¹ for the inner capillary tip, whereas pure ethanol was fed at 0.3 cm³ h⁻¹ by the outermost one. The tip-to-collector distance was 30 cm and the electrical potential difference was 24 kV (the collector was at -12 kV and the tips at +12 kV). Thermo-stabilization and carbonization were carried out in a horizontal tubular furnace (150 cm³ gas (STM) min⁻¹) under different conditions described in the text and figures. Particularly, the effect of heating variables during stabilization, and that of the atmosphere used in the stabilization and carbonization steps have been studied. Finally, some of the resulting carbonized fibers were analyzed by different techniques.

For comparison purposes, equivalent powdery carbon materials were also prepared from lignin powder without the electrospinning step. For such a purpose, H₃PO₄ (85 wt %)/lignin/ethanol solutions (n/1/1 weight ratios, with n = 0; 0.3; and also 0.8), identical to those used for electrospinning, were dried for 24 h at 60 °C. Next, the stabilization and carbonization conditions were similar to those utilized for the fibers. The P-containing carbonized fibers and powders were washed with distilled water at 60 °C to remove weakly-anchored P species, and dried overnight at 80 °C prior to characterization.

The as-spun, stabilized and carbonized fibers are referred to as AF, SF and CF for the pure lignin fibers, respectively. In the case of the preparation of carbon fibers by chemical activation with H₃PO₄ (impregnation ratio of 0.3), the fibers are referred to as PAF, PSF and PCF. In the case of stabilized fibers, the heating rate (0.08; 1 or 3 °C min⁻¹) or the particular use of N₂ atmosphere is also reflected in the nomenclature. For carbonized fibers, the stabilization conditions (without P: 0.08 °C min⁻¹ up to 200 °C + 60 h at 200 °C; with P: 1 °C min⁻¹ up to 200 °C + 1 h at 200 °C) are not specified and only the particular use of N₂ atmosphere for stabilization (N₂-PCF) or the oxidizing one for carbonization (PCF-3%O₂) are considered in the nomenclature. The carbonized lignin powders are designated as AC (in reference to conventional activated carbons (ACs)), followed by a number (n) indicating the aforementioned H₃PO₄ weight ratio (n = 0; 03 for 0.3 or 08 for 0.8) in the H₃PO₄/lignin/ethanol (n/1/1) solutions.

Characterization of activated carbon fibers

SEM and TEM images were obtained by a JEOL JSM-6490LV microscope (at 25 kV voltage) and a Philips CM200 microscope (at an accelerating voltage of 200 kV), respectively. Raman spectra were recorded with a RENISHAW micro-Raman system using an Ar⁺ laser at 514 nm as the excitation source with a

spectral resolution of 2 cm^{-1} . The textural properties were characterized by physical adsorption of gases (N_2 at $-196 \text{ }^\circ\text{C}$ and CO_2 at $0 \text{ }^\circ\text{C}$) in a Micromeritics ASAP2020. Samples were previously outgassed for 8 h at $150 \text{ }^\circ\text{C}$ under vacuum. The mechanical properties were measured as non-aligned multi-fiber carbon meshes, in a DEBEN Microtest (2KN Tensile). Temperature-programmed desorption (TPD) experiments were performed in a tubular vertical furnace and the amounts of CO and CO_2 evolving groups were monitored by NDIR analyzers (Siemens; ULTRAMAT 22 model). X-ray photoelectron spectroscopy (XPS) data were registered by a 5700C model Physical Electronics apparatus with Mg $K\alpha$ radiation (1253.6 eV). For the analysis of XPS peaks, the maximum signal was set at 284.5 eV . The fitting of the XPS peaks was done by least squares using Gaussian–Lorentzian peak shapes. For thermogravimetric analysis (TG), a CI Electronics MK2 balance and samples between 10 and 15 mg were used.

The catalytic decomposition of 2-propanol was studied in a fixed bed reactor as previously reported,²³ with 70 mg of carbon fibers, a 2-propanol partial pressure of 0.018 atm in inert atmosphere and a space time of $0.055 \text{ g s } \mu\text{mol}^{-1}$. The concentrations of 2-propanol and products were analyzed by on line gas chromatography (490 micro-GC equipped with PPQ, 5A molsieve and Wax columns, Agilent). $\gamma\text{-Al}_2\text{O}_3$ (Puralox 150/200 from Sasol) was used as a reference acid catalyst. The electrochemical characterization was carried out in a standard three-electrode cell in different electrolytes by using a Pt wire as counter electrode and a $\text{Ag}/\text{AgCl}/\text{Cl}(\text{sat.})$ electrode as the reference one (Electrochemical Analyzer 600D Series, CH Instrument Inc.). To be used as binderless electrodes, the

carbon fibers were manually compressed in between two stainless steel meshes (current collectors).

Result and discussion

Preparation of electrospun phosphorus-functionalized carbon fibers

Phosphoric acid-containing lignin fibers were prepared by electrospinning of H_3PO_4 /lignin/ethanol (0.3/1/1 wt ratio) solutions in ethanol. The as-spun H_3PO_4 /lignin fibers show diameters ranging from 400 nm to $3 \text{ } \mu\text{m}$ (PAF in Figure 1), mostly $\leq 1 \text{ } \mu\text{m}$. Since the presence of H_3PO_4 increases the viscosity and electrical conductivity of the lignin/ethanol solutions, promoting whipping instability,^{14,15} more curly fibers were observed when compared with H_3PO_4 -free ones (AF and PAF in Figure 1).

The electrospun fibers were subjected to a thermo-oxidative stabilization step prior to carbonization in order to increase the glass transition temperature of lignin and thus prevent fibers from partial or total fusion. The heat-treatment was carried out under air or inert (N_2) atmosphere ($150 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$) and different heating rates up to a temperature of $200 \text{ }^\circ\text{C}$, and this final temperature was kept for different times (1 or 60 hours). As shown in Figure 1, in the absence of H_3PO_4 the stabilization must be necessary slow ($0.08 \text{ }^\circ\text{C min}^{-1}$ to $200 \text{ }^\circ\text{C} + 60 \text{ h}$ at $200 \text{ }^\circ\text{C}$) (SF-0.08-200-60) to maintain a high glass transition temperature, preventing fibers from fusion.¹⁶

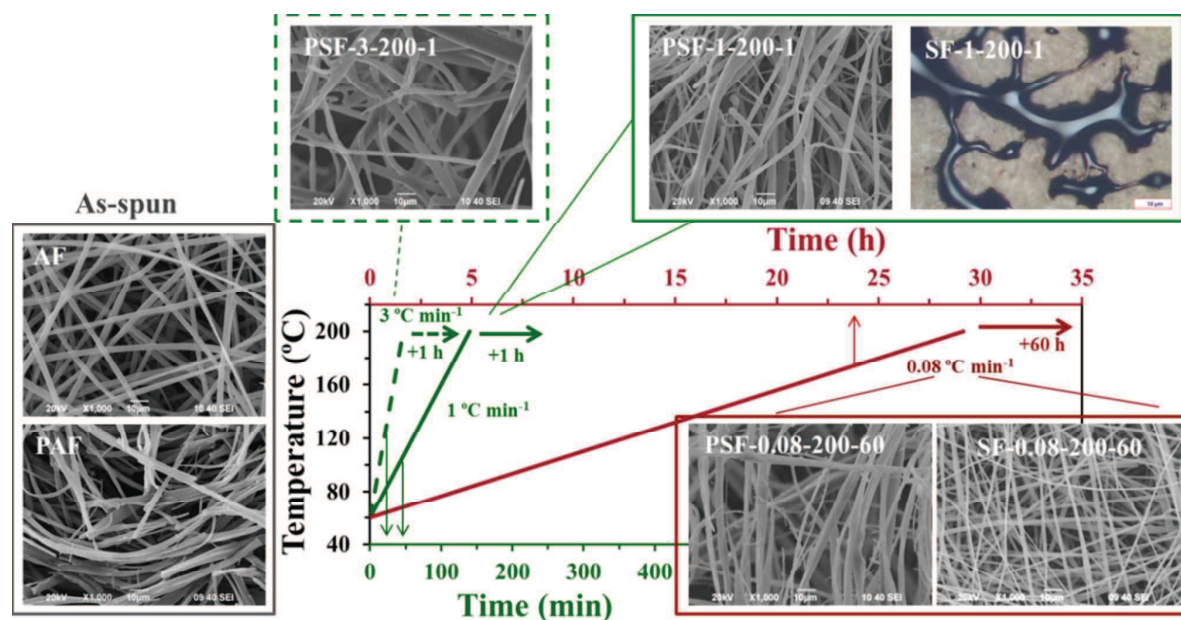


Figure 1. Effect of the heating rate (HR) on the morphology (SEM images) of the air-stabilized lignin fibers with (PSF-HR) and without (SF-HR) H_3PO_4 . This Figure also shows the images of the corresponding as-spun fibers (PAF and AF, respectively)

Hence, faster heating rates such as $1\text{ }^{\circ}\text{C min}^{-1}$ produce complete fusion of pure lignin fibers (SF-1-200-1 in Figure 1). By contrast, and apart from a conventional long stabilizations process (PSF-0.08-200-60 in Figure 1), the presence of H_3PO_4 allows using heating rates as high as $1\text{--}3\text{ }^{\circ}\text{C min}^{-1}$ without producing partial fusion or swelling of the fibers (PSF-1-200-1 and PSF-3-200-1 in Figure 1). Thus, electrospun H_3PO_4 /lignin fibers can be stabilized in only 1 h and 45 min, whereas the pure lignin fibers require more than 90 h, what entails a remarkable time reduction (50-60 times) of the thermostabilization treatment.

Furthermore, the stabilized fibers showed similar diameter to that of the as-spun ones and the incorporation of H_3PO_4 increased the stabilization yields from 76% for SF-0.08-200-60 to 83 wt % for PSF-0.08-200-60.

Table 1 shows the weight surface concentration obtained from XPS analysis for lignin-based fibers before and after stabilization in inert or oxidizing atmospheres, where an increase in the oxygen content after stabilization in air is observed for both prepared fibers. The increase in the oxygen content after stabilization step is expected to be low due to the high oxygen content of the raw lignin. Nevertheless, this increase in the oxygen content is notably lower in the case of the lignin fibers prepared with phosphoric acid, given that the oxygen content was already increased during the preparation of these P-containing fibers (PAF).

Figure 2 shows the O1s, C1s and P2p spectra of as spun and stabilized lignin fibers without and with phosphoric acid. In the case of as spun lignin fibers, a band centered at about 532.6 eV can be observed in the O1s spectrum, corresponding to oxygen as in C-OH and C-O-C bonds (Figures 2b and d). However, the band is more intense and narrower for the phosphoric acid-containing lignin fibers (PAF in Figure 2d), which can be ascribed to the presence of oxygen in C-O-P bonds, as in phosphate and polyphosphates surface groups.²⁴ Stabilization in air of lignin fibers caused a significant modification of the profiles for the O1s and C1s spectra (SF-0.08-200-60 in Figure 2a and b), widening the O1s band at lower binding energies, at about 531 eV (Figure 2b), as a consequence of formation of oxygen as in C=O bond.

Table 1. Weight surface concentration by XPS of as spun and stabilized lignin fibers

Samples	Weight surface concentration by XPS (%)		
	C	O	P
AF	73.4	26.6	--
SF-0.08-200-60	68.0	32.0	--
SF-0.08-200-60-N ₂	83.6	16.4	--
PAF	64.5	28.2	7.3
PSF-1-200-1	64.1	29.5	6.4
PSF-1-200-1-N ₂	63.4	28.3	8.3

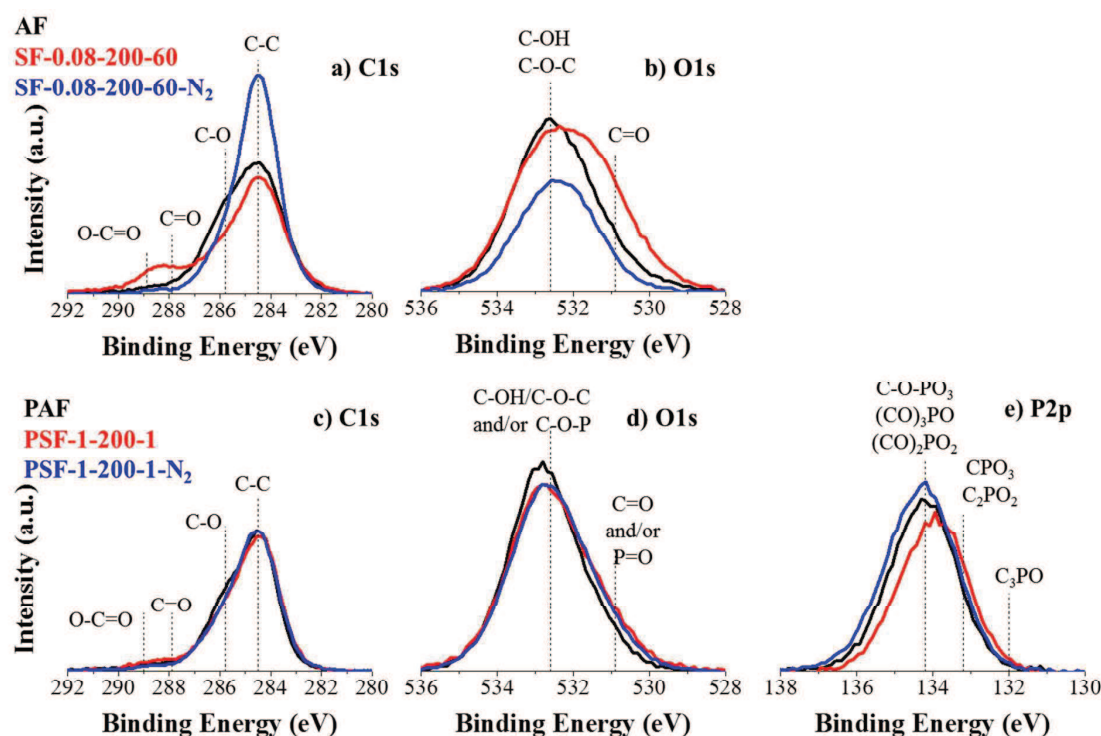


Figure 2. XPS spectra of C1s, O1s and P2p core-levels of as-spun and stabilized fibers under oxidizing and inert atmosphere. (a, b) pure lignin fibers, (c – e) phosphorus lignin fibers.

In the case of phosphorus-containing lignin fibers, the oxidative stabilization process did not produce such a notable change on these profiles, leading only to a slight reduction of the band observed at 532.6 eV and to the appearance of a small tail at 530.9 eV (Figure 2d), which can be associated to oxygen as in C=O bond or even as in P=O one. For the case of stabilization of lignin fibers, a noticeable band (or a shoulder of the C-C band located at 284.5 eV) can be observed in the C1s spectrum from approximately 287.5 to 290.8 eV (Figure 2a), which indicates the presence of C=O and/or O-C=O bonds. However, this small band at 288.2 eV is not clearly observed after stabilization of P-containing lignin fibers (Figure 2c), suggesting that the small tail of the O1s spectrum for this sample, at about 530.9 eV, may correspond to P=O bond instead of C=O one. In this sense, Figure 2e presents the P2p spectra for PAF and PSF-1-200-1 that show a band with a main peak at a binding energy around 134 eV, characteristic of pentavalent tetracoordinated phosphorus, as in phosphates and/or polyphosphates.^{20,21,25-28} A slightly shift of this band to lower binding energy and a small reduction of the band area can be

appreciated after stabilization of the phosphorus-containing lignin fibers (PSF-1-200-1 in Figure 2e), which evidences slight modifications of the state of P in the lignin structure after the stabilization treatment, producing some phosphorus in a more reduced state as in C-PO bonds, as a consequence of dehydration and cross-linking reactions.

These results are in agreement with other studies. The increase in the oxygen content during oxidative stabilization of lignin fibers is related to the incorporation of mainly carbonyl and carboxylic surface structures at low temperature, which can be incorporated into anhydride and ester groups,^{9,10,16} generating cross-links within the lignin fibers structure. In the case of phosphorus containing lignin fibers, the increase of oxygen content after stabilization is lower than that observed for the pure lignin fibers (Table 1). Figure 3 and 4 show, respectively, a scheme of the Alcell lignin structure adapted from the lignin structure proposed by Adler²⁹ and the scheme of the structure that we propose for this lignin after reaction with H₃PO₄ (with approximately the same chemical composition of PAF).

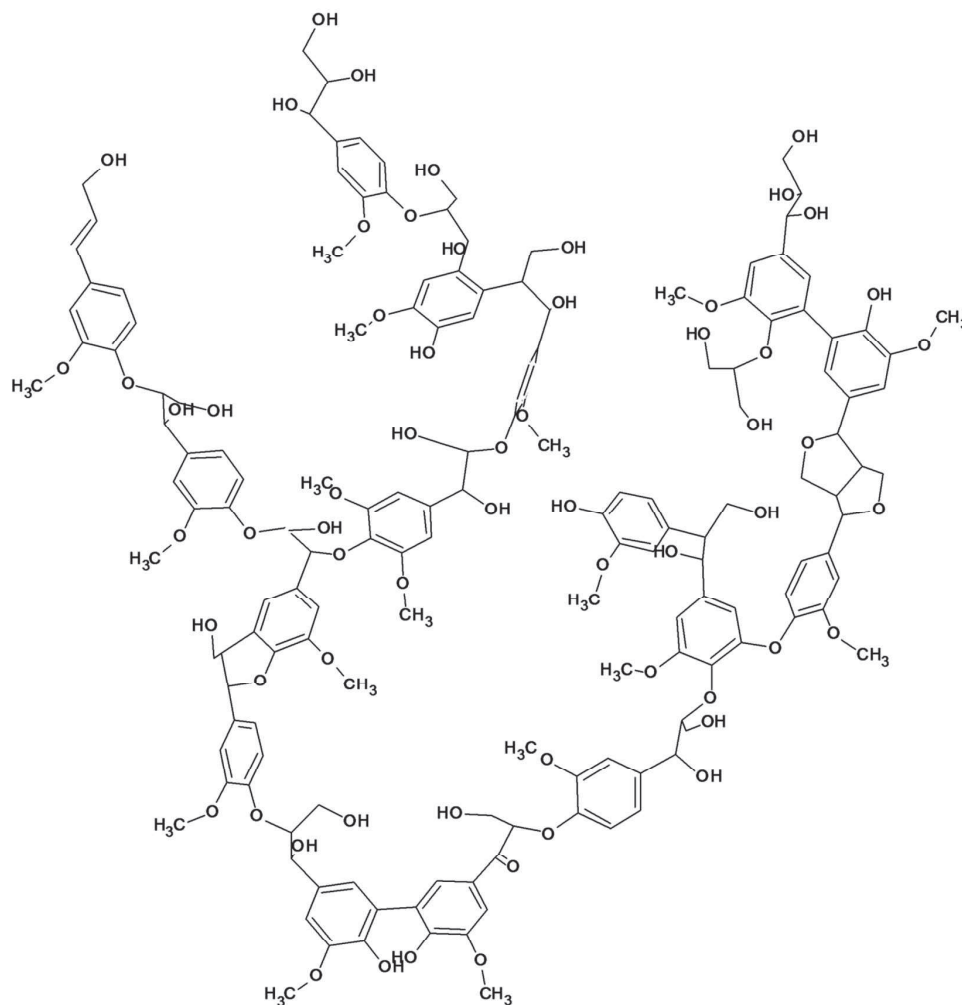


Figure 3. Alcell lignin structure adapted from the lignin structure proposed by Adler²⁹

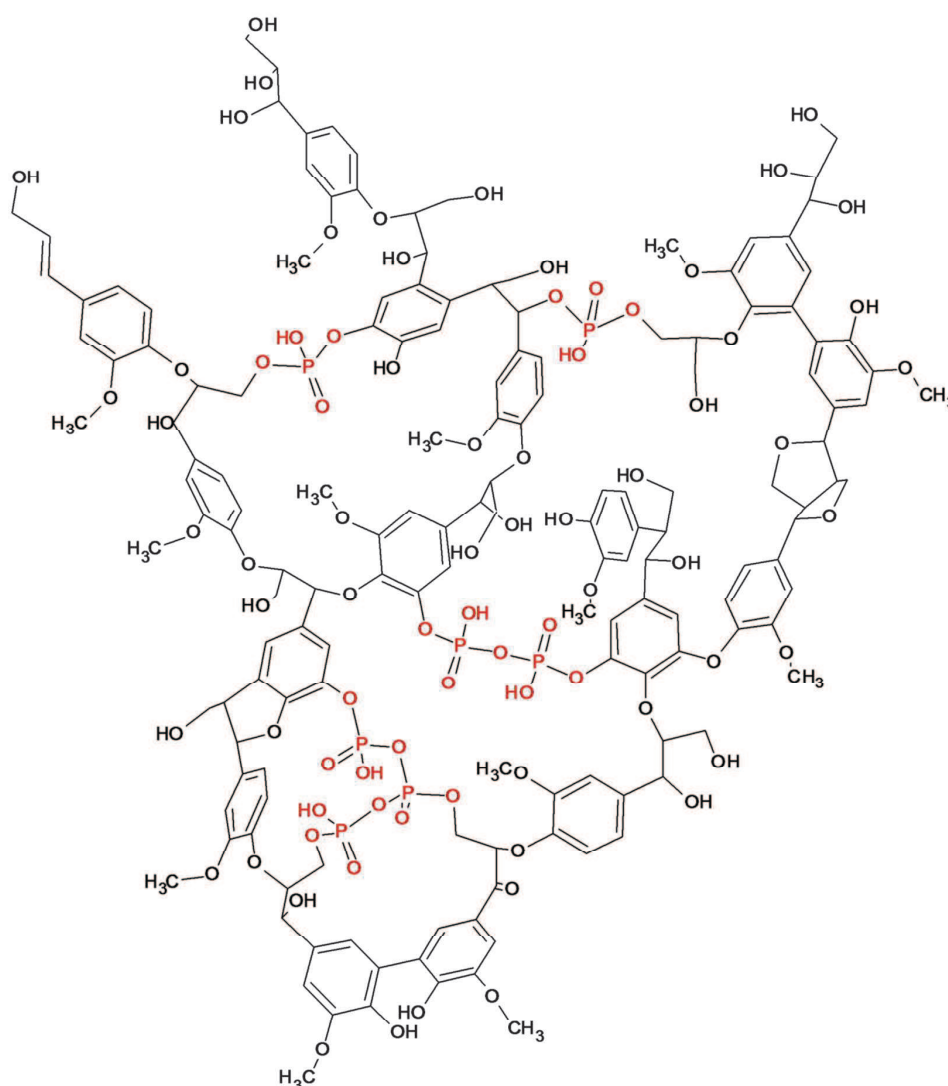


Figure 4. Alcell lignin structure, proposed in this work, after reaction with H_3PO_4 (C = 71.6 %at, O = 25.6 %at, P = 2.8 %at).

The incorporation of H_3PO_4 to the initial lignin solution produces more oxidized spun lignin fibers (PAF), but of the whole lignin fiber matrix in this case, due to the reaction of phosphoric acid with the dissolved lignin, generating phosphate (and/or polyphosphate) esters throughout the structure of lignin fibers.^{20,21} These phosphate groups have been found to be very active for surface carbon oxidation, even at room temperature^{24,26} and thus seems to be the responsible for the production of cross-linking reactions that are, in this case, very active and effective in increasing the glass transition temperature of the lignin fibers, reducing the time needed for the stabilization step and improving this process. On the contrary, the oxidative stabilization of the lignin fibers in the absence of phosphoric acid takes place on the surface of the fibers and, in this case, oxygen has to diffuse to the inner part, the core, of the lignin fiber matrix to form cross-linkage that favour higher glass transition temperatures to prevent fibers from fusion during the carbonization/activation process, which is only possible with much slower heating rates.

With the aim to study if phosphate and polyphosphate esters, generated during reaction of lignin with H_3PO_4 , are enough to prevent the fusion of phosphorus-lignin fibers the stabilization step has been carried out under inert atmosphere (N_2). Under this inert atmosphere, a complete fusion of the pure lignin fibers is produced, even at low heating rates (Figure 5a), indicating that the stabilization of pure lignin fibers necessarily requires oxidation of the carbonaceous fiber matrix in order to increase the glass transition temperature and prevent fiber from fusion.¹⁶ A clear decrease in the oxygen content is observed when the lignin fibers are stabilized under inert atmosphere (Table 1). The XPS analysis of the lignin fibers stabilized in N_2 (SF-0.08-200-60- N_2) reflects a decrease the C–O bond contribution (a clear shortening in the intensity of the band at 286.0 eV in C1s spectrum, Figure 2a) and a clear reduction of the whole O1s band spectrum (Figure 2b). These results confirm that the heat treatment of pure lignin fibers in N_2 atmosphere only produces the release of oxygen functional groups (mainly by decomposition of certain oxygenated compounds),

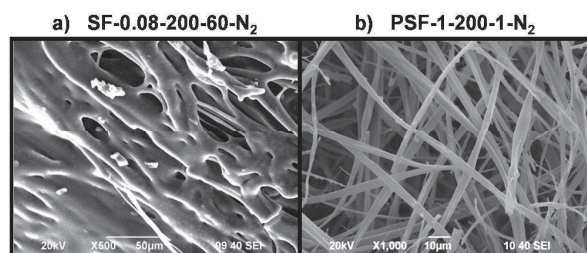


Figure 5. SEM images of stabilized lignin fibers, SF and PSF, under inert atmosphere

without generating oxidation or cross-linking reactions, avoiding any possibility of stabilization and producing the fusion of the fibers during the subsequent carbonization step, for the production of carbon fibres (Figure 5a). XPS characterization of phosphorus containing lignin derived fibers shows almost no differences (Table 1, Figure 2c-e), having the as-spun and the air and inert stabilized phosphorus-lignin fibers practically identical surface composition. Therefore, the presence of thermally stable phosphate and/or polyphosphate esters allows also the stabilization of electrospun lignin fibers even under inert atmosphere (N_2) at relatively high heating rates (1 or 3 $^{\circ}C$ min^{-1} , Figure 5b). Thus, these phosphate and polyphosphate species generate cross-links with the lignin structure without the need to incorporate oxygen from the gas phase.

The stabilized materials were heat-treated at 10 $^{\circ}C$ min^{-1} up to 900 $^{\circ}C$ under inert (N_2) or oxidizing (3 vol % O_2 in N_2) atmospheres. The influence of phosphorus-functionalization and the atmosphere on the weight loss during carbonization was studied by thermogravimetric analysis (Figure 6a). In agreement with our previous works, stabilized pure lignin fibers can be carbonized at

900 $^{\circ}C$ under inert conditions with a 37 % yield (SF- N_2 in Figure 6a) (27 % total yield, considering stabilization + carbonization).^{9,10} On the other hand, the presence of P species in the stabilized lignin fibers increases the carbonization yield up to 48 % (40 % total yield) (PSF- N_2), by favoring the restriction of tars formation during the carbonization process and dehydration reactions produced at high carbonization temperatures, increasing the carbon content.^{20,30} Regarding the oxidation or combustion behavior, while pure lignin fibers suffer from total combustion at 700 $^{\circ}C$ in an atmosphere of 3 % of O_2 (SF- $3\%O_2$), a 18 % of the initial lignin weight remains as carbon fibers after heating up to 900 $^{\circ}C$ when phosphorus is present (15 % total yield, PSF- $3\%O_2$). It has been found that during the relatively high-temperature (700 - 900 $^{\circ}C$) carbonization process of phosphoric acid-treated lignocellulosic materials different phosphorus groups (C-O-PO, C-PO type) remain thermally stable bonded to the surface of the final carbon matrix, being these P-surface groups responsible of the high oxidation resistance and acid character of the carbon surface.^{20,24,30} Thus, phosphorus carbon fibers can be produced at 900 $^{\circ}C$ even in an oxidative atmosphere (O_2 3 %), due to the presence of phosphorus surfaces groups that are incorporated to the carbon fiber matrix during the carbonization step.

As a consequence of such versatile methodology, due to the presence of phosphorus groups in the lignin structure, the thermal processing of as-spun fibers into lignin-based carbon fibres can be carried out through not only the conventional 2 steps-route, stabilization (air) + carbonization (N_2) (route a, Scheme 1), but also under 2 new combinations (routes b and c, Scheme 1), as well as directly in a single step under inert (route d, Scheme 1) or oxidizing atmosphere (route e, Scheme 1). This allows to produce carbon fibers with a wider variety of properties and, in the case of a single step (route e, Scheme 1), with a notably process time reduction, in only 2 h 40 min (total thermal processing).

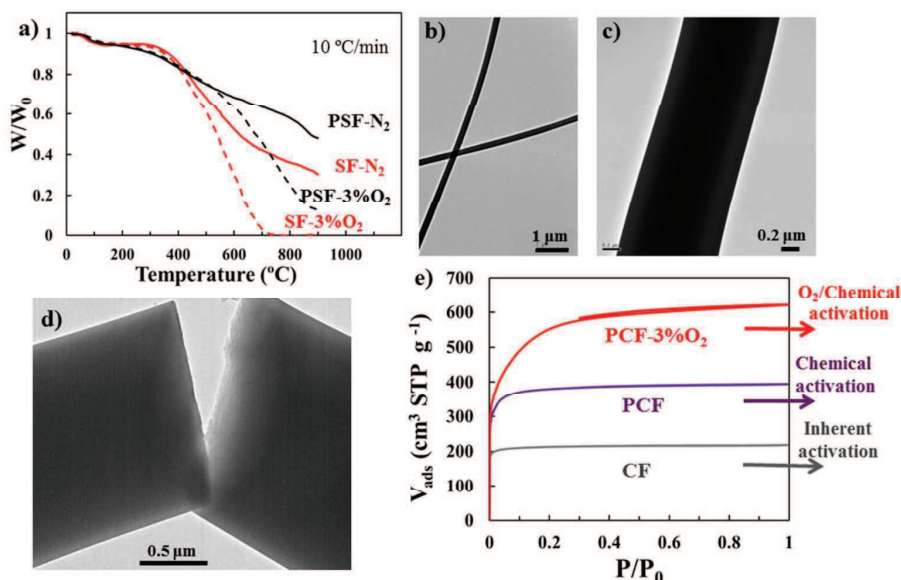
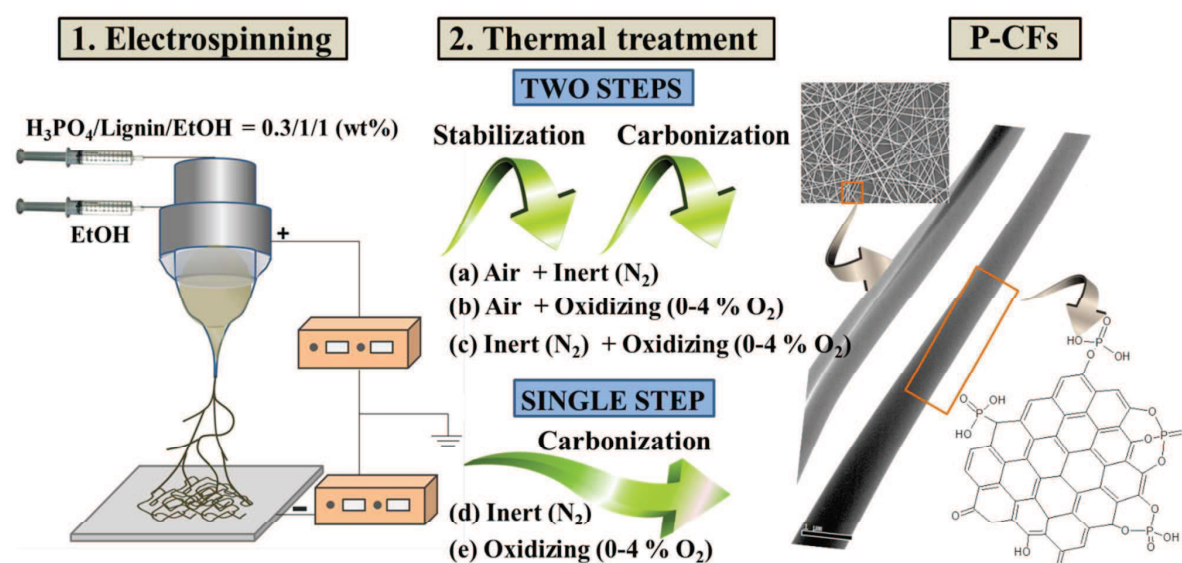


Figure 6. (a) Weight-loss of air-thermostabilized lignin fibers (SF and PSF correspond to SF-0.08 and PSF-1 samples, respectively) during heating up to 900 $^{\circ}C$ under inert (N_2) or oxidizing (3 vol % O_2) conditions. (b,c,d) Different TEM images of PCF sample; and (e) N_2 adsorption-desorption isotherms (-196 $^{\circ}C$) of different carbon fibers.



Scheme 1. Scheme of the phosphorus carbon fibers preparation by electrospinning of lignin solution, representing the two- and single-step thermal routes in which the stabilization and carbonization of the fibers could be carried out under different or similar atmosphere conditions, respectively.

Textural properties.

The phosphorus carbon fibres display quite similar diameters to those of the as-spun and stabilized ones, mainly ranging between 400 nm (Figure 6b) to 1 μm (Figure 6c), and an apparently smooth surface with no microscopic defects, even at ending zones (Figure 6d). Textural characterization points out that the carbonization of pure lignin fibers (CF) produces a well-defined microporous structure, as deduced from the type-I shape of the N_2 adsorption isotherm (Figure 6e), and a high specific surface area, of around $850 \text{ m}^2 \cdot \text{g}^{-1}$ (Table 2). In particular, the higher CO_2 -micropore volume, if we compared it with that derived from the adsorption of nitrogen ($V_{\text{DR}}(\text{CO}_2) > V_{\text{t}}(\text{N}_2)$) indicates the presence of narrow micropores (diameters below 0.7 nm).³¹ This large development of microporosity has already been ascribed to the high oxygen content of lignin,^{9,10} which may be a key factor during devolatilization in the carbonization process, namely, the oxygen-driven inherent activation of lignin fibers. The carbonization of phosphorus electro-spun fibers (PCF) results in carbon fibers with a substantially higher surface area (ca. $1350 \text{ m}^2 \cdot \text{g}^{-1}$) and microporosity, with a higher proportion of wider micropores ($V_{\text{t}}(\text{N}_2) > V_{\text{DR}}(\text{CO}_2)$) (see Table 2). These effects on the porous texture may be attributed to the H_3PO_4 -chemical activation process upon heating,^{17,20,30,32,33} although the atmosphere of the stabilization process plays a key factor in the development of porosity in the final carbon fibers. Actually, for phosphorus-containing carbon fibers derived from phosphorus-lignin fibers that have been stabilized under N_2 atmosphere (N_2 -PCF; see Table 2) no effect on the activation of the lignin fibers has been detected (similar porous texture observed for CF and N_2 -PCF; Table 2), which suggests that

oxygen incorporation during air stabilization seems to be of paramount importance for the chemical activation of the fibers. It has been reported that the phosphate- and/or polyphosphate-carbon structures may favour oxygen spillover,^{24,34,35} by adsorption of molecular oxygen on the P surface complexes and migration of activated oxygen species from these P groups to the carbonaceous matrix. After the oxidative stabilization step, this activated oxygen in the fiber carbonaceous matrix may partially gasify the structure of the fibers during the carbonization process, developing a larger porosity and surface area in the final carbon fiber than if no oxygen is used during the stabilization process. In the case of phosphorus-containing lignin fibers stabilized in inert atmosphere and under the experimental conditions used in this study (relatively low $\text{H}_3\text{PO}_4/\text{lignin}$ mass ratio), the oxygen supplied by the phosphate (and/or polyphosphate) ester groups to the lignin fibers matrix appears to act just producing cross-linking reactions during the stabilization process to avoid fusion of the fibers and it does not seem to be available during the further carbonization step to activate the carbonaceous fiber matrix, with no further added development of porosity of the final carbon fibers.

On the other hand, the carbonization of stabilized P-functionalized fibers under an O_2 -containing atmosphere up to temperatures as high as $900 \text{ }^\circ\text{C}$ (Figure 6a) further induces an additional porosity development (PCF-3% O_2 in Figure 6e and Table 2). This O_2 activation at high temperatures produces phosphorus carbon fibers with apparent surface areas of ca. $2000 \text{ m}^2 \cdot \text{g}^{-1}$ (3-fold increase compared to pure lignin derived carbon fibers), a wider microporosity and the presence of mesopores (around a 10 % of total pore volume; see Table 2).

Table 2. Porous texture parameters (calculated as reported elsewhere¹⁰) and mass surface composition for the studied lignin-based carbon fibers. For comparison purposes, the table also includes the data of activated carbons (AC) powders prepared from lignin:H₃PO₄:ethanol precursor solutions, without the electrospinning step.

Sample	N ₂ adsorption				CO ₂ adsorption		XPS mass surface concentration		
	A _{BET} ^[a] m ² g ⁻¹	A _t ^[b] m ² g ⁻¹	V _t ^[c] cm ³ g ⁻¹	V _{meso} ^[d] cm ³ g ⁻¹	A _{DR} ^[e] m ² g ⁻¹	V _{DR} ^[f] cm ³ g ⁻¹	C %wt	O %wt	P %wt
AC0	86	0.4	0.033	0.005	514	0.206	92.1	7.9	0.0
AC03	719	6	0.282	0.009	825	0.331	87.4	10.2	2.4
AC08	1177	18	0.507	0.002	844	0.338	87.8	9.4	2.8
CF	850	7	0.329	0.006	1001	0.401	96.3	3.7	0.0
PCF	1348	25	0.580	0.009	1027	0.412	90.5	7.7	1.8
N ₂ -PCF	869	6	0.342	0.005	675	0.271	90.3	6.2	3.4
PCF-3%O ₂	2000	112	0.849	0.107	1021	0.409	81.2	16.0	2.8

[a] A_{BET} is the apparent surface area. [b] A_t is the external surface area. [c] V_t is the micropore volume. [d] V_{meso} is the mesopore volume. [e] A_{DR} is the narrow micropore surface area. [f] V_{DR} is the narrow micropore volume.

It has been reported that stable C-O-P type surface groups decompose to C'-P type surface groups at temperatures higher than 700-750 °C, with formation of gaseous CO (C' represents a new surface carbon site), and that in the presence of molecular oxygen this C'-P surface groups are (re)oxidized to C'-O-P, where the P-surface groups act as inhibitors for the surface carbon gasification at temperatures lower than 700-750 °C (enhancing the oxidation resistance of the carbon fiber) and as a selective gasification agent or catalyst at temperatures higher than 700-750 °C (production of surface C''-P and gaseous C'O and again (re)oxidation to C'''-O-P).²⁴

The robustness of the carbon fibers is an important property even for functional applications. The degree of structural ordering in the phosphorus carbon fibers was followed by Raman spectroscopy. In spite of the higher porosity of these phosphorus carbon fibres, the quite similar spectroscopic features obtained for PCF and PCF-3%O₂ samples compared to that of CF (prepared from pure lignin) (Figure 7 and Table 3) suggests that the P functionalities may induced or promote certain structural ordering.^{36,37} The Raman spectra of the carbon fibres (Figure 7) show two main broad and overlapping bands, at about 1350 and 1600 cm⁻¹, the former being associated to the E_{2g} vibration mode of the ideal graphitic lattice (G band), and the later characteristic for disordered carbon (D band).^{9,10,38,39}

These spectra were deconvoluted as reported so far,^{10,39} and the spectral parameters are collected in Table 3. The Raman shift (ν) of G band, the full width at half maximum ($\Delta\nu$) of D and G bands and the intensity ratio (I_D/I_G) of the fibers carbonized at 900 °C under inert atmosphere are independent

of the P functionalization. Nevertheless, the noticeable narrowing of D band could point out a lower contribution of structural disorder in phosphorus carbon fibers. On the contrary, the shift of G band towards larger wavenumbers, as well as the increase in the G band width and in the I_D/I_G ratio observed for the highly porous phosphorus carbon fibers (PCF-3%O₂) are all Raman features characteristic of a less ordered structure.^{38,39} This is in accordance with their much more developed microporosity (see Table 2).

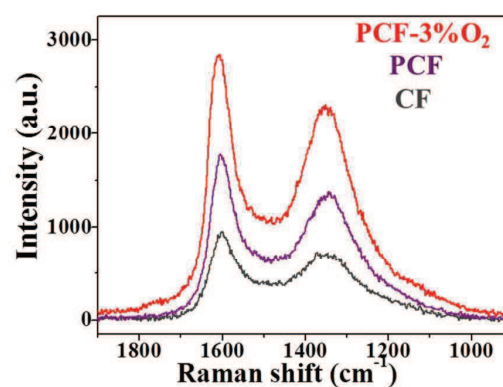


Figure 7. Raman spectra of various lignin-based carbon fibers

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Table 3. Raman parameters determined from the deconvolution of first-order Raman spectra of different lignin-based carbon fibers.

Sample	ν_G (cm ⁻¹)	$\Delta\nu_G$ (cm ⁻¹)	$\Delta\nu_G$ (cm ⁻¹)	I_D/I_G
CF	1599	67.3	182.8	0.87
PCF	1600	67.3	153.9	0.88
N ₂ -PCF	1600	57.7	153.9	0.89
PCF-3%O ₂	1607	71.6	144.3	0.94

Mechanical properties are also of great importance even for functional application carbon fibers. Table 4 shows different values of Young's Modulus and tensile strength of non-porous and activated carbon fibers compared with the carbon fibers prepared in this work. In this sense Dallmeyer et al.⁴⁰ found that the inter-fiber bonding improve the mechanical properties of the carbon fibers, reporting tensile strength and Young's modulus values of 75 MPa and 4 GPa, respectively, for bonding fibers carbonized at 1000 °C with a relatively poor development of porosity (BET surface area of 400 m²·g⁻¹). On the other hand, Uraki et al.⁴¹ studied the effect of the surface area on the tensile strength of carbon fibers obtained from softwood acetic acid lignin. They found a decrease in tensile strength value from 150 to 100 MPa when the carbonized fibers were activated under steam flow for different times, obtaining BET surfaces areas from 370 to 1930 m²·g⁻¹. Tensile strength values of 250-300 MPa and Young's modulus values of 2-4 GPa have been obtained for the carbon fibers prepared in this work. In spite of these values are lower than those reported for non-porous carbon fibers obtained from kraft lignin for structural applications,^{42,43} the small carbon fibers diameters obtained by electrospinning of lignin solution make the carbon materials thus prepared more mechanically resistant than other carbon fibers prepared from lignin or other lignocellulosic precursor. In this sense, it is noteworthy to highlight that these mechanical properties are not sufficient for structural applications. However, they are unusually high in such porous materials of small diameter and enough suitable for functional application such as in adsorption and heterogeneous catalysis and as electrodes, etc.

Chemical properties.

As shown in Table 2, the incorporation of P to the lignin-based carbon fibers increases the surface oxygen content by XPS from 4 wt % for CF to 8 wt % for PCF and from 6.2 wt% for N₂-PCF to 16 wt % for PCF-3%O₂ when carbonization is carried out under inert or oxidizing atmosphere, respectively. On the other hand, the amount of surface phosphorus on the P-containing carbon fibers was found to vary from 1.8 to 3.5 wt % P by XPS (Table 2). The mass surface concentration of P determined by XPS of the PCF sample (1.8 wt% P) is quite similar to that obtained by Inductive Coupled Plasma (ICP) (1.5 wt% P), indicating that P is well distributed along the surface (internal and external) of the final carbon fiber. The nature and relative contribution of the different O and P

functionalities on phosphorus carbon fibers was further investigated from the XPS spectra and TPD profiles (Figure 8). The C1s region of XPS spectra was deconvoluted into 4 contributions (see an example in Figure 8a). Apart from a main contribution due to the aromatic -C-C- bonds formed upon carbonization, the phosphorus carbon fibers present a remarkable contribution of single-bonded -C-O- and/or -C-P- species (285.8 eV), as well as some -C=O and -COOH and/or -COOR species (at 287.9 and 289 eV, respectively).⁴⁴ On the other hand, the XPS-P2p spectrum of phosphorus carbon fibers (Figure 8b) shows a broad band centered at ca. 133 eV, characteristic of strongly-attached P-species in activated carbons prepared at high temperatures.^{17,20,30,32,33} This spectrum can be deconvoluted into 3 doublets corresponding to 3 different surface groups of P functionalities: polyphosphates and/or phosphates (referred to as -C-O-P- species: (CO)₃PO, (CO)₂PO₂ and (CO)PO₃) at 134.0 eV; -C-P-O- species (C-PO₃ and/or C₂-PO₂ groups) at 133.2 eV; and the major contribution, -C₃PO groups, at 132.0 eV.²⁴ From the TPD profiles of Figures 8c and 8d it can be clearly discerned that the amount of CO-evolving groups (Figure 8c) in highly activated phosphorus carbon fibers is considerably much higher than that of CO₂-evolving ones (Figure 8d). In particular, the CO profiles of PCF fibers are characterized by a sharp rise from 500 °C to 700 °C, which can be attributed to decomposition of phenol, ether and/or carbonyl groups. The TPD CO evolution from 700 and up to 950 or 1000 °C, presenting a maximum at 860 °C, for different carbons prepared by chemical activation of lignocellulosic materials with phosphoric acid has been attributed to the decomposition of C-O-P types bond of C-O-PO₃, generating C'-PO₃ surface groups, where C' refers a new surface carbon atom.^{24,32}

Table 4. Young's Modulus and tensile strength values for carbon fibers prepared in this work and for other carbon fibers reported in the literature.

Sample	A _{BET} (m ² ·g ⁻¹)	Tensile strength (MPa)	Young's Modulus (GPa)	Ref.
CF	855	303	4	This work
PCF	1345	248	2	This work
BF-1000	411	74	4	40
BF-800	435	76	2	40
BF-600	456	58	2	40
SAL-ACF	370	150	--	41
SAL-ACF-80	1390	100	--	41
HWKL	--*	422	40	42
Alcell	--*	388	40	42
Lignin	--*	605	61	43

*non-porous carbon fibers

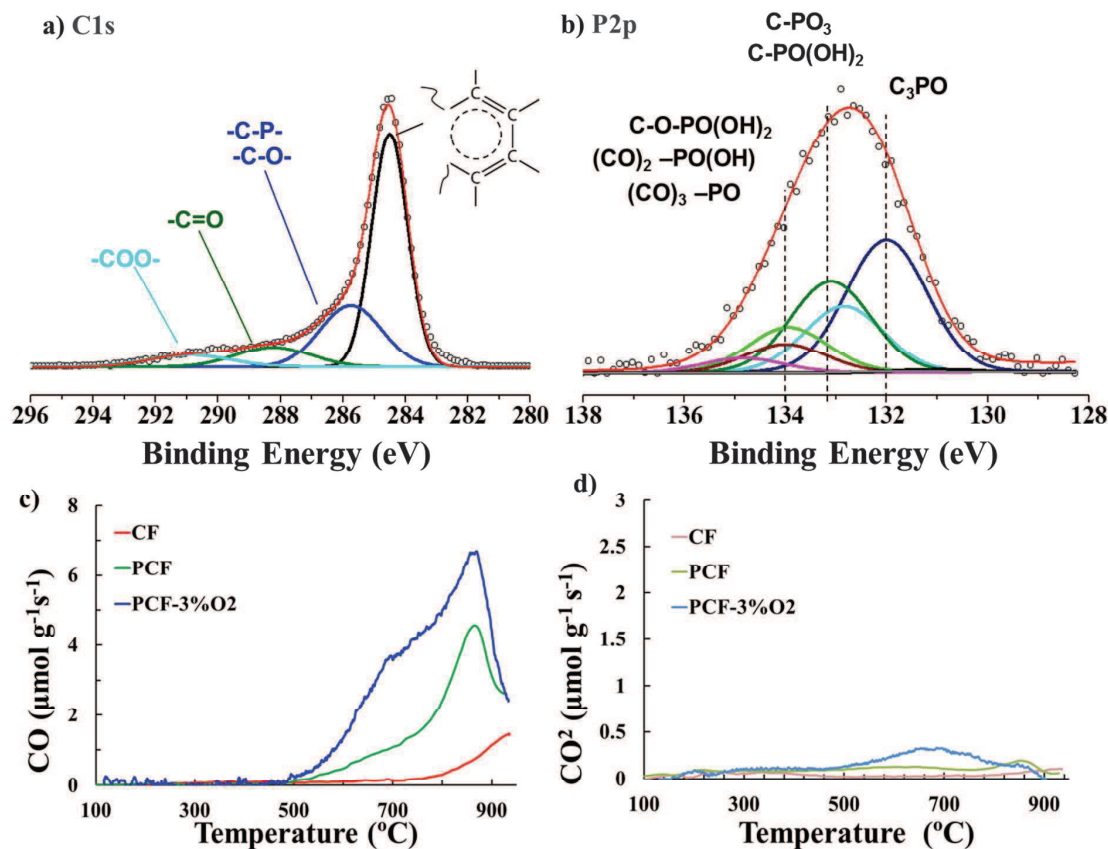


Figure 8. (a) C1s and (b) P2p XPS deconvoluted spectra of PCF-3%O₂ fibers; (c) CO and (d) CO₂ evolution during TPD experiments of CFs with and without P.

This higher content in phenols, ethers and/or carbonyl groups and –C–O–P– surface species greatly agrees with the functionalities distribution observed by XPS (Figure 8a and 8b) and it is also found in other less oxidized samples (PCF and N₂-PCF) (Figures not shown). CF (without P) presents a much lower evolution of CO and CO₂.

The profiles for these two gases indicate that these sample mainly contain quinone- and/or carbonyl-like surface groups evolving as CO above 700 °C (Figure 8c),⁴⁵ i.e., a poor surface chemistry characteristic of carbon materials prepared at high temperatures under inert atmosphere.

The distribution of phosphorus species on the different carbon fibers was analyzed by X-ray energy dispersive spectroscopy (XEDS) (Figure 9). CF displays a negligible blank P signal (Figure 9a). However, the much higher intensity and density of P signals on the selected area together with the increased and constant intensity of P signals across the width of PCF (Figure 9b) indicate that the phosphorus functionalities are uniformly distributed throughout this P-containing sample.

Properties for interfacial applications

The functionalization of submicron lignin fibers with phosphorus species plays a decisive role in the length reduction and versatility

of the hereby reported new method for production of functional carbon fibers.

The promotion of stabilization is quite advantageous to shorten the carbon fibers production time. This is simply achieved by adding a small amount of H₃PO₄, which reacts with lignin to generate –C–O–P bonds as in phosphate (and/or polyphosphate) ester groups. Previous strategies on optimizing the stabilization of fibers from lignin or other biopolymers have been focused on new extraction routes, physical and/or chemical modification treatments and/or the incorporation of polymer additives,^{43,46–48} what usually entails more complex and expensive procedures. Other approaches were based on stabilizers or precursors different to H₃PO₄ or lignin, respectively.^{49,50}

Activated and functionalized carbon fibers can be directly prepared, without additional impregnation/drying and/or post-functionalization steps. In order to achieve very high specific surface areas (2000 m² g^{–1}) and a large amount of functional groups, conventional carbon fibers would necessarily require of additional chemical (NaOH, KOH, H₃PO₄, ZnCl₂, etc.) that in many cases damages the morphology and structure of the fibers and/or physical (CO₂ or steam water at 800–900 °C) activation processes,^{1,11–13,51,52} and liquid- or gas-phase oxidation post-treatments.³⁴

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In order to emphasize the extent of activation produced by phosphoric acid in the electrospun lignin fibers, powdery activated carbons with different impregnation ratios were prepared, for comparison purposes, without the aid of electrospinning (see experimental section). In agreement with this result, considerably much higher activating agent contents (from 10 to 20 times) are usually necessary to produce the chemical activation degree observed for the phosphorus carbon fibers reported in the present work (see Table 2),^{1,17,32,33,51,52} which is attributed to the uniform distribution of the reactant phosphorus species through the entire fibers matrix obtained by the methodology proposed in this work.

The benefits of the aforementioned textural and chemical characteristics of phosphorus carbon fibers were analyzed for practical application. Firstly, it is well-known that the large surface-to-volume ratio and endless form of fibrous structures promote excellent mass transfer properties, low pressure drop, ease of handling and reduced inter-particle boundaries that, compared to other morphologies (powder, granular, pellet, etc.), offer several advantages for heterogeneous catalytic reactions, adsorption and separation processes, electrochemical applications, etc.¹⁻⁴

In catalysis. The catalytic behavior of the different carbon fibers was analyzed for the 2-propanol decomposition reaction. This is a test reaction for the evaluation of the acid and basic properties of heterogeneous catalysts.^{23,53,54} It is generally accepted that the reaction conversion increases with the surface acidity (or basicity) of the catalyst and that 2-propanol mainly dehydrates to propylene (PP) over acid

sites, whereas it decomposes through dehydrogenation over basic sites, yielding acetone (Ac).

Figure 10a represents the 2-propanol conversion as a function of temperature over various lignin-based carbon fibers with and without P used as catalysts. The conversion increases with the reaction temperature for all the catalysts. In particular, whereas CF shows total conversion at 600 °C, the P-containing carbon fibers catalysts exhibit conversions of 100 % between 300 and 370 °C and their activity increases with the phosphorus surface content (N_2 -PCF \approx PCF-3%O₂ > PCF).

The selectivity of the P-containing carbon fibers towards the production of PP increases rapidly with temperature, so that it is higher than 90 % above 200 °C (Figure 10b). On the opposite, for CF the selectivity changes towards Ac (100%) even at conversions as low as 15 % (at 415 °C). The high conversions and selectivities to PP found for the P-containing carbon fibers maybe attributed to the presence of Brønsted acid sites of surface P groups,^{23,53,54} highlighting their acidic character. On the contrary, the production of acetone is indicative of the presence of basic sites on CF.

The catalytic performance of the lignin-based phosphorus carbon fibers was compared to that of commercial γ -Al₂O₃ (powder), which is among the most studied acid catalysts. Phosphorus carbon fibers present almost comparable catalytic activity for 2-propanol dehydration (Figure 10a), as well as similar selectivity towards PP (Figure 10b) to that of γ -Al₂O₃ catalyst. Nevertheless, it is necessary to increase the temperature at least 30 °C to get the same conversion.

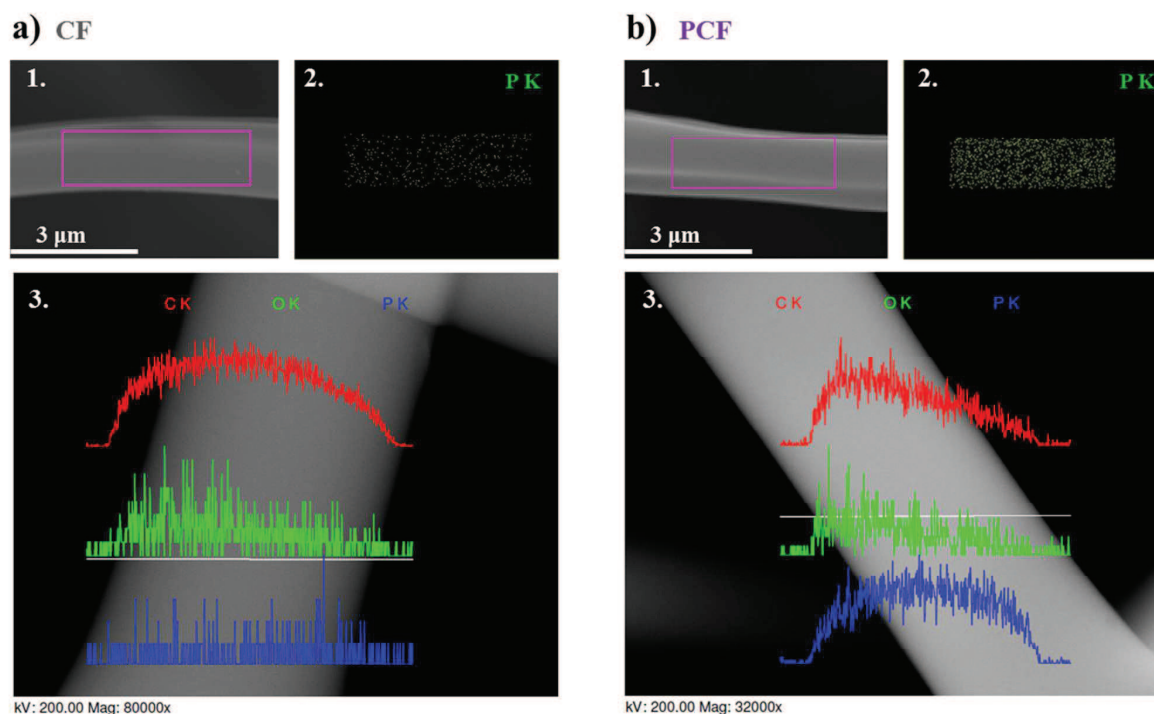


Figure 9. Two (1,2) and one (3) dimensional distributions of P and other species (O, C) on different lignin-based carbon fibers, as determined by XEDS.

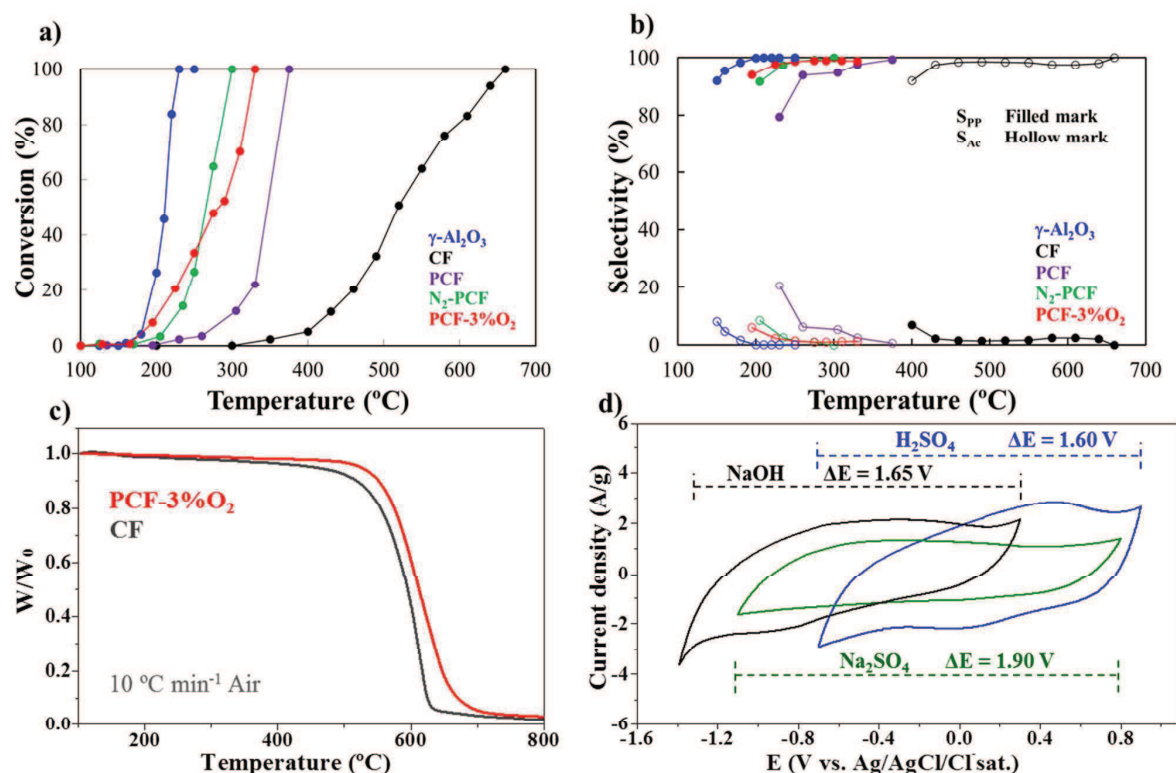


Figure 10. (a) Evolution of 2-propanol (2-PrOH) conversion and (b) selectivity to propylene (S_{PP}) and acetone (S_{Ac}) as a function of temperature for various lignin-based carbon fibers and a commercial reference material ($\gamma\text{-Al}_2\text{O}_3$) used as catalysts (Reaction conditions: $P_{2\text{-PrOH}} = 0.018$ atm in He; Space time $(W/F)_{2\text{-PrOH}} = 0.055$ g s μmol^{-1}). (c) Non-isothermal oxidation profiles in air of lignin-based carbon fibers with and without P and. (d) Steady-state voltammograms of PCF in different electrolytes (concentration = 0.5 M; scan rate = 10 mV s⁻¹).

On the other hand, beside surface acidity, a high oxidation resistance is also a required property of carbon materials for their potential use as catalysts and catalyst supports in several reactions involving oxygen at moderate temperatures (200–400 °C).^{1,2,17,23,30,32,33,53,54} Thus the thermal stability of the catalysts under oxygen atmosphere becomes crucial. Figure 10c shows the non-isothermal air oxidation profiles of lignin-based carbon fibers with and without P. Although CF show a remarkable oxidation resistance by itself, the fibers start to lose weight (oxidize) slowly from 350–400 °C to 500 °C, temperature at which they quickly combust. The P-containing carbon fibers, however, do not suffer from any weight-loss until 525–550 °C, showing an increased oxidation resistance induced by the high thermal stability of the P surface groups in the presence of molecular oxygen, already reported in the literature.^{20,24,25,30}

In adsorption. Because of their high surface area and versatile physico-chemical properties, porous carbons constitute one of the most efficient and broadly used materials as adsorbents.^{55–59} The fine diameter (≤ 1 μm) of the P-containing carbon fibers prepared in this work,^{56,57} together with their network of

mesopores and wider micropores (Table 2) may enormously enhance the accessibility and fast diffusion of molecules to the inner microporous structure.^{58,59} The benefits of these properties were confirmed for the adsorption of phenol in aqueous solutions, obtaining adsorption capacities of around 180 mg·g⁻¹ for PCF (at 25 °C and 25 mg L⁻¹). These values are higher than those found, at the same adsorption conditions, for activated carbons prepared by conventional physical and chemical activation.^{19,60}

In electrochemical applications. As electrode materials, carbons are generally required to show a high conductivity and surface area, as well as adequate chemical and electrochemical stability in different electrolytes. The basic electrochemical features of the phosphorus carbon fibers were tested, directly as binderless electrodes, by conventional cyclic voltammetry in a three-electrode cell. The straight shape and large current densities observed in the voltammograms of the self-standing PCF (Figure 10d) clearly reflect their suitable conductivity and great potentiality for electrochemical applications.

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Another feature of upmost importance is the electro-chemical stability. It is related to the range of electrode potentials (potential window (ΔE)) at which neither the electrode nor the electrolyte suffer from electrochemical decomposition.

As observed in Figure 10d, the phosphorus carbon fibers (see as an example the PCF fibers) show no oxidation currents up to 0.90 V, 0.30 V or 0.80 V in the acid, basic or neutral electrolytes, respectively.

This result points out that PCF presents a high electro-oxidation resistance, i.e. they can operate safely up to very high potentials, stressing their potential application in supercapacitors, fuel cells, (bio)sensors, electrosynthesis, etc.⁶¹⁻⁶³ On the other hand, PCF starts to display reduction currents at very low potentials on the negative side (below -0.7 V, -1.35 V or -1.1 V in the acid, basic or neutral electrolytes, respectively), at which the electrochemical H storage and/or H₂ evolution occurs.^{64,65} The observed enhanced electro-oxidation resistance⁶⁶ and low potentials for the electrolyte decomposition⁶⁷ have been attributed to the presence of surface P functionalities in carbons.

As a consequence, PCF exhibits wide stability potential windows: $\Delta E = 1.60$ V, 1.65 V or 1.90 V in H₂SO₄, NaOH and Na₂SO₄, respectively, which are probably among the widest ever reported for aqueous electrolytes (ΔE values for porous carbons are usually around 1.00 V). Such a high electrochemical stability induced by P functionalities has been found beneficial for energy storage in supercapacitors.^{67,68} Moreover, the high surface area and microporosity of PCF, together with its small diameter and the presence of mesopores are well-known properties of carbons for an optimum ion adsorption and fast diffusion, respectively, for this application.^{63,69} Although a detailed study is not the aim of the present work, the energy density of these materials in a supercapacitor (SC) device can be predicted from the equation $E = 0.5 \cdot C \cdot V^2$; where C is the cell capacitance and V is the operating voltage. Considering that in a symmetric SC (2-electrodes cell) the maximum capacitance is a fourth of that calculated by using a 3-electrode cell (from the voltammograms of Figure 10d, these values are around 150-200 F g⁻¹) and that the operating voltage can be optimized to approach the aforementioned stability potential windows (1.90-1.60 V), symmetric SCs using PCF electrodes could potentially display energy densities of 15-20 W h kg⁻¹. These energy densities are 2-5 times higher than those shown by commercial activated carbons in organic electrolytes and similar to those of hybrid Li-ion capacitors. Hence, taking into account the excellent performance of lignin-based carbon fibers as electrodes for supercapacitors,⁶⁹ the obtained PCF, which exhibits considerably better stability and larger surface area, constitute a promising low-cost electrode candidate for energy storage.

Conclusions

A new versatile route to prepare advanced functional carbon fibers in remarkably short time, from an abundant and renewable polymer like lignin, has been reported. The route

implies the electrospinning of H₃PO₄/lignin solutions to produce in only one-step submicron-diameter P-functionalized lignin fibers, in which the phosphorus functionalities produce unique effects on their thermal processing, enabling to shorten the conventional stabilization process to avoid fiber fusion from more than 90 h to only 2 h or even to stabilize the lignin fibers in inert atmosphere. The incorporation of H₃PO₄ to the initial lignin solution produces more oxidized spun lignin fibers, due to the reaction of phosphoric acid with the dissolved lignin, generating phosphate (and/or polyphosphate) esters throughout the structure of the lignin fibers. These phosphate groups seems to be the responsible for the production of cross-linking reactions during the stabilization step that are, in this case, very active and effective in increasing the glass transition temperature of the lignin fibers, reducing the time needed for the stabilization step and improving this process. Moreover, they promote the chemical activation of lignin fibers and greatly increase their oxidation resistance, avoiding their complete combustion during carbonization under low concentration of O₂ at temperatures as high as 900 °C. The resulting carbon fibers gather different interesting properties, such as sub-micron diameters (≤ 1 μm), large surface area (≈ 2000 m² g⁻¹), relatively high performance in relation to their mechanical properties for functional applications and a rich variety of uniformly-distributed O and P surface functionalities, which make them very attractive for heterogeneous catalysis, adsorption and electrochemical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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TABLE OF CONTENT

Phosphorus functionalization for the rapid preparation of highly nanoporous submicron-diameter carbon fibers by electrospinning of lignin solutions

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Rapid preparation of low-cost carbon fibers by electrospinning of lignin solutions thanks to the functionalization with H_3PO_4 .