How does phosphoric acid interact with cherry stones? A discussion on overlooked aspects of chemical activation

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Abstract

The fabrication of activated carbon (AC) is widely carried out by the so-called chemical activation method, in which the biomass substratum is put in touch with an impregnating chemical agent prior to the carbonization stage. Even though this methodology is known for a long time, there are many features that are still poorly understood, particularly those regarding the details of the underlying mechanisms implied during the interaction of the activating agent with the precursor, eventually leading to the development of AC. Previous research conducted in the laboratories dealt with the use of cherry stones (CS) and phosphoric acid, towards ACs with tailored porous structures, finding out that the experimental variables of the impregnation stage

were crucial for their eventual characteristics. Thus, the results obtained at that time deserved further discussion, with the aim at unraveling the true nature of those findings. With such purpose, we herein deepen into the use of CS and H_3PO_4 in non-conventional impregnation methodologies, performed in the previous works. Four series of H_3PO_4 -impregnated products were prepared in a previous research, using a wide range of impregnation strategies, aiming at controlling the loading of H_3PO_4 on the lignocellulosic substratum. Herein, by only staring at the mass uptake upon impregnation and subsequent drying, it was possible to link the uptake with the chemical changes of H_3PO_4 in agreement with essential chemistry knowledge. Mass gain is strongly dependent on the impregnation method, and interesting insights arise on the basis of the mass changes of CS after impregnation.

1. Introduction

Lignocellulosic biomass includes materials such as agricultural residues, forestry residues, portions of municipal solid waste, and various industrial wastes (Palonen et al. 2004). It is a low cost and abundant resource with a great potential to support large-scale production of fuels and chemicals. Valuable materials such as activated carbon (AC) can also be prepared from lignocellulosic biomass (Danish and Ahmad 2018). AC is a synthetic kind of porous material that possesses high adsorption ability thereby being an extremely versatile adsorbent of gases, vapours, and chemical species in solution (Danish et al. 2017). Because of its adsorption properties, AC is used as adsorbent, catalyst and support for catalysts (Tsoncheva et al. 2018). AC is usually prepared by one of the well-known two-stage methods of physical or chemical activation. In the chemical method, the selected precursor is usually impregnated with an activating agent in the first place, such as H_3PO_4 in aqueous solution, and the

resulting product is then carbonized under specific heating conditions (Danish et al. 2014). Frequently, impregnation is carried out in two successive steps of soaking and drying by heating below and above the boiling point of water, respectively. In the impregnation stage, H_3PO_4 interacts chemically and physically with the precursor and as a result changes occur in the chemical composition of the system which will influence not only the impregnation process but also the subsequent carbonization, and ultimately the porous structure of the final product.

The principal biopolymeric components of lignocellulosic biomass are hemicelluloses, cellulose and lignin. In addition, it contains extractives (i.e. oils, fats, etc.) and trace amounts of inorganic compounds and metal ions (Horvath et al. 2010). Hemicelluloses are mixtures of polysaccharides synthesized in wood almost entirely from glucose, mannose, galactose, xilose, arabinose, 4-*O* methylglucuronic acid, and galactorunic acid residues (Pettersen 1984). Structurally, xylose, mannose and galactose are found as monomeric fragments in the hemicellulose backbone chain, and arabinose, galactose, and 4-*O*-methyl-d-glucuronic acid in hemicellulose side chains (Pettersen 1984). Cellulose is the main constituent of plant cell wall conferring structural support. It is a glucan polymer consisting of long, linear parallel chains of 1,4- β -bonded anhydroglucose units. The molecular chains pack in layers that are held together by weak van der Waals forces (Pettersen 1984). In cellulose chains, hydroxyl groups form intra- and intermolecular hydrogen bonds, as displayed in Figure 1a (Pettersen 1984; Negahdar et al. 2016), as displayed in Figure 1a. Chemically, lignin is a phenolic substance derived mainly from three alcohols with a different degree of methoxylation (i.e., coniferyl, sinapyl and p-coumaryl alcohols), which are connected with different types of ethers and carbon-carbon bonds (Boerjan et al. 2003).

On the other hand, lignocellulosic biomass includes fruit stones that possess a hardened endocarp are called drupes. These fruit stones are formed by lignification of the fruit endocarp layer (Dardick et al. 2010). Lignification is the process of producing the lignin polymer from lignin monomers via enzymatic oxidative reactions aided by peroxidases and laccases. Previous studies indicate that lignification begins in the second stage of fruit development until maturity. Furthermore, the biochemical analysis of a wide series of drupes has shown that they contain nearly twice as much lignin as wood (Dardick and Callahan 2014). Chemical structures for hemicelluloses and lignin have frequently been reported before in the literature (Pettersen 1984, Jagtoyen and Derbyshire 1998, Chávez-Sifontes and Domine 2013, Oinoen et al. 2015, Baipai 2016, Negahdar et al. 2016).

Among the above mentioned biopolymers, hemicelluloses are not crystalline, soluble in alkali and easily hydrolyzed by acids. The solubility of cellulose is hindered as it is covalently, intimately associated with lignin and hemicelluloses (Pettersen 1984). Since the cellulose structure consists of crystalline and amorphous domains (Pettersen 1984), the crystalline one constituting the major proportion, only a minor portion of this biopolymer is soluble in substances such as acids. As far as lignin is concerned, partial digestion by acid action occurs (Jagtoyen and Derbyshire 1998). By acid-catalyzed hydrolysis, hemicellulose chains eventually convert into five and six carbon sugars and cellulose chains into six carbon sugar (glucose) by Reactions (1) and (2) (Wyman 2013; Satarn et al. 2014):

and resulting monosaccharides may undergo dehydration and transform into furan ring containing compounds such as furfural and hydroxymethylfurfural (HMF), as shown in Fig. 1b (Ek et al. 2009).

Fig. 1. a) Representation of the structure and intramolecular hydrogen bonding of cellylose, b) Chemical changes produced as a result of the hydrolysis of cellulose and hemicelluloses.

When H_3PO_4 is specifically used in the treatment of lignocellulosic materials, the hydrolysis of hemicelluloses and cellulose is more or less severe depending on the acid concentration (Nguyen et al. 2009; Agbor et al. 2011). With 1-10 % H_3PO_4 under

mild heating conditions, hydrolysis mainly concerns the hemicellulosic fraction as the cellulosic fraction is not affected to an appreciable extent (Gómez et al. 2004, 2006). However, anhydrous H_3PO_4 is an excellent direct solvent for cellulose. The dissolving power of this acid is very strong with dissolution occurring within a few minutes. As a result, even 38% (w/w) cellulose solutions can be prepared (Boerstoele et al. 2001). After the acid hydrolysis, the extraction of lignin can be performed from the residual liquid and solid phases (Horvath 2006; Tsubota et al. 2015). Figure 2 depicts the changes originated in the structure of biomass by acid treatment (Hsu et al. 1980; Kumar et al. 2009). The residual liquid from the hydrolysis of sugar cane bagasse with dilute H_3PO_4 is constituted of sugars (xylose, glucose and arabinose), products of decomposition of the hemicelluloses (such as oligomers from the polymers and acetic acid generated from the hydrolysis of acetyl groups linked to sugars) and of the monosaccharides released (such as furfural, product of dehydration of pentoses, and HMF, and products of dehydration of hexoses). In the concentration of the mixture obtained by evaporation not only water but also small amounts of reaction products (e.g. growth inhibitors such as acetic acid, furfural and HMF) are removed (Gómez et al. 2004, 2006; citations therein). Using dilute H_3PO_4 in the treatment of commercial cellulose prior to heating at high temperature Dobre et al. (2003) concluded that the extent to which levoglucosenone is formed depends on the cellulose crystallinity and the degree of dehydration. With concentrated acids, however, the dissolution leads to a hydrolytic cleavage of the cellulose chains, and the cellulose molecules are transformed to derivatives, such as esters (Horvath 2006).

Fig. 2. General overview experienced by lignocellulosic biomass upon treatment with acids. Reprinted with permission from reference (Kumar et al. 2009). American Chemical Society © 2009.

Another process variable with influence on the chemical changes produced in lignocellulosic materials by treatment with H_3PO_4 solution is the soaking temperature (Solum et al. 1995). The reaction of white oak wood with 30% H_3PO_4 at low temperatures between 50 and 170 °C principally promotes dehydration and also chemical changes such as loss of carboxyl and methyl groups from hemicelluloses, formation of ketone groups (possibly by the formation of levoglucosenone) and ester groups from amorphous cellulose, the formation of phosphate esters (see Fig. 3; Jagtoyen and Derbyshire 1998), initiation of crosslinking reactions, development of aromaticity and loss of aliphatic, carboxyl and carbonyl groups, and significant alteration of the lignin structure. When heating at high temperatures, the H_3PO_4 was found to promote an expansion of the wood structure above the range of 250-450 °C with an associated development of porosity and creation of an extensive surface area. Above 450 °C, a secondary dimensional contraction paralleled the reduction in porosity (Solum et al. 1995).

Fig. 3. Reaction of phosphoric acid (in red) with glucose units (contained in cellulose) giving rise to phosphate ester bonds, at low temperatures.

When H_3PO_4 alone is heat-treated, pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), metaphosphoric acid (HPO_3) and phosphorus pentoxide (P_2O_5) are successively formed as temperature rises. However, the heat treatment of a lignocellulosic material (e.g. yellow poplar) with such a chemically modified H_3PO_4 gives rise to the formation of ester linkages with $-\text{OH}$ groups on cellulose at temperatures below 200°C , attachment of small polyaromatic units mostly by phosphate and polyphosphate bridges at 280°C , and scission of P-O-C bonds at higher temperatures (Jagtoyen and Derbyshire 1998). These chemical changes involving phosphorus acids are accompanied by the formation of crosslinks between the polymer chains, occurrence of cyclization and condensation reactions leading to an increase in aromaticity and in the size of the polyaromatic unit, and cleavage of crosslinks leading to a very extensive growth of the size of the aromatic units (Jagtoyen and Derbyshire 1998). With H_3PO_4 -impregnated cherry stones, a great increase in weight loss was observed between 625 and 900°C as compared to the starting material, this being connected with the gasification of carbon atoms by P_2O_5

and thermal decomposition of polyphosphoric acids with the formation, in both instances, of white phosphorus (P_4) as a reaction product (Olivares-Marín et al. 2006).

With a view to preparing AC with a tailored porous structure, several impregnation strategies of a lignocellulosic material such as cherry stones, CS (i.e. an agro-industrial by-product generated in abundance in a large number of European countries like Turkey, Italy and Spain), were devised and the associated mass changes have been reported before (González-Domínguez et al. 2011, 2017). Such strategies not only included the use of H_3PO_4 solutions of different concentrations but also of further diluted or over-concentrated H_3PO_4 solutions, and also the use of thermally modified CS. In other strategies, impregnation is effected in a single impregnation step, instead of in two steps (impregnation and drying) as in the usual method, and the filtered residues are either washed with distilled water or reused as the impregnation solution. The present study aims at unravelling the underlying mechanisms ruling the impregnation process in agreement with physical and chemical changes undergone by the H_3PO_4 impregnation solution and lignocellulosic substratum after soaking and drying steps.

2. Experimental

2.1. Materials and Methods

Cherry stones (CS) from Valle del Jerte (province of Cáceres, Spain) were used as the AC precursor. As-received, CS was first air dried and then milled and sieved, the particle size between 1 and 2 mm being chosen. Data of the chemical analyses obtained for CS are compiled in Table 1 (Durán-Valle et al. 2005). The lignocellulosic composition of CS is: hemicelluloses 14.7%; cellulose 29.4%; lignin 30.7%, and its empirical formula is $CH_{1.52}O_{0.62}N_{0.006}$ (González et al. 2003). For comparison purposes,

biopolymer compositions for other fruit stones and for lignocellulosic materials such as wood, are compiled in Table 2. The elsewhere reported thermogravimetric analysis of CS (Olivares-Marin et al. 2006) in inert atmosphere (under a N₂ flow) showed two weight loss effects between 30-200 °C and 200-300 °C. The former with a mass loss of 8.28 wt.% was associated with the release of moisture and a small fraction of volatile components from CS. The latter with a mass loss of 17.93 wt.% was ascribed to the thermal decomposition of less stable chemical constituents of CS (Olivares-Marin et al. 2006), chiefly hemicelluloses (Baquero et al. 2003; Carvalho et al. 2002; Girgis and Ishak 1999; Himmel et al. 2007; Lim et al. 2010; Mantanis et al. 1994; Stamm 1934, 1964; Yang et al. 2007). After sizing, CS were cleaned and conditioned by soaking overnight in diluted sulphuric acid (5% v/v), thoroughly rinsed with distilled water (until neutral pH), and oven-dried at 120°C for 24 h.

Table 1: Chemical analyses of CS

Ultimate	wt. %	Proximate	wt. %
Carbon	49.00	Moisture	5.41
Hydrogen	6.37	Volatile matter	71.72
Nitrogen	0.24	Ashes	0.24
Oxygen	44.15	Fixed carbon	22.63

Table 2: Biopolymer composition of lignocellulosic materials (wt.%)

Scientific Name	Description	Hemicelluloses	Cellulose	Lignin	Reference
<i>Prunus avium</i>	Cherry stones	14.7	29.4	30.7	(González et al. 2003)
<i>Olea europea</i>	Olive stones*	21.9	31.9	26.5	(Heredia et al. 1987)
<i>Phoenix dactylifera</i>	Date stones	18	42	11	(Bouchelta et al. 2008)
<i>Populus tremuloides</i>	Aspen wood	20 - 35	40 - 50	15 - 30	(Horvath 2006)
	Tree wood	65 - 75		18 - 35	(Pettersen 1984)
	Forestry waste	20 - 35	35 - 50	15 - 25	(Wyman 1994)

* On a dry basis scale.

Commercial H_3PO_4 reagent grade (85% PA-ACS-ISO, Panreac) was used. Because of its very polar character, the H_3PO_4 molecule is highly soluble in water, i.e. 548 g H_3PO_4 /100 g H_2O at 25 °C (Lide 2005). It behaves like a tribasic acid, K_1 being $7.11 \cdot 10^{-3}$ at 25 °C (Greenwood and Earnshaw 1989). K_1 decreases with temperature as concentration increases. H_3PO_4 tends to bond by intermolecular hydrogen bridges, aggregation and condensation. As a last resort polyphosphoric acids of general formula $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$, with n up to 17, are formed as a complex mixture of linear molecules of various chain lengths (Toy 1973). The P_2O_5 concentrations to which orthophosphoric, pyrophosphoric and polyphosphoric acid correspond are 72.4, 79.6 and 84.0 wt.%, respectively, whereas compositions in between the first and the second concentrations are referred to as superphosphoric acid (Boerstoele et al. 2001). The formation of molecular aggregates in the solution gives rise to an increase in viscosity, decrease in vapor pressure, and increase in boiling point with the rise in concentration. As a guide, viscosity (cP) at 20 °C is 2.6 for 30 wt.% H_3PO_4 solution and 47.0 for 85 wt.% H_3PO_4 solution. The vapor pressure (mm Hg) at 25 °C is 21.19 for 29.80 wt.% H_3PO_4 solution and 3.86 for 80.14 wt.% H_3PO_4 solution (Greenwood and Earnshaw 1989). Finally, boiling point ranges between 100.2 and 108.0 °C for 10-50 wt.% H_3PO_4 solution and is 150 °C for the 85 wt.% H_3PO_4 solution (Toy 1973).

N_2 adsorption isotherms were measured in Autosorb-1 (Quantachrome) instrument, and the surface area was determined as reported in González-Domínguez et al. (2017).

X-ray photoelectron spectroscopy (XPS) measurements were carried out in a K-Alpha Thermo Scientific equipment under high vacuum conditions ($2 \cdot 10^{-7}$ mbar). A monochromatic radiation of 1486.68 eV (Al K_α line) was used to irradiate samples

perpendicularly at 12 kV. Additionally, a flood gun device (working at 4.2 mA) compensated for the load losses. The register settings were established as 50 ms accumulation time for each step in all cases. Survey spectra were recorded by 1 eV energy steps and 20 scans.

2.2. Impregnation strategies

Scheme 1 fully depicts the whole scenario undergone to carry out impregnation of CS with phosphoric acid. Two H_3PO_4 solutions were used as stocks. One was a diluted (D) solution and the other was a concentrated (C) solution, and contained 16 g H_3PO_4 /100 mL water and 144.5 g H_3PO_4 /100 mL water, respectively. In fact, commercial H_3PO_4 without further dilution was used as C. Solutions of the same H_3PO_4 concentrations were also used in a previous study (Olivares-Marín et al. 2006). In a typical impregnation experiment, as described in more detail elsewhere (González-Domínguez et al. 2011), 100 mL of H_3PO_4 solution were first brought into contact with about 25 g of CS in a beaker and the system, under steady magnetic stirring, was heated at 85 °C for 2 h. To prevent unwanted solvent losses by evaporation, the beaker was maintained sealed with a latex film throughout the entire process. Then, the resulting liquid/solid mixture was oven-dried at 120 °C for 24 h. For the sake of brevity, the first and second impregnation treatments are referred to as FIT and SIT hereafter. As a whole, four series of impregnated products (IPs) were prepared (see Table 3 and Scheme 1).

Scheme 1. General preparation process of H_3PO_4 -impregnated CS

Table 3: Experimental conditions, sample nomenclature and mass changes upon impregnation (reproduced with permission from (González-Domínguez et al. 2011), © Elsevier 2011).

[H ₃ PO ₄] g/100 mL	t/h	NI	Filtering	Washing	T/°C	IP codes	Series	Δm/g
16						D	1	7.30
5.33						DL1		1.20
5.33		2				DL2		1.85
10.66						DI1		4.43
5.33		3				DL3		2.30
16			Yes			DF	2	1.34
16			Yes	Yes		DFW		0.48
n-d						DRL		n-d
144.5	0					C0	3	135.54
	2					C2		143.20
	6					C6		126.29
	12					C12		127.45
	24					C24		134.96
16					200	S200D	4	9.09
16					300	S300D		15.04
144.5					200	S200C		132.80
144.5					300	S300C		94.36

Abbreviations: *n-d*, not determined; *t*, oven-drying time; *NI*, number of successive impregnations; *T*, semi-carbonization temperature.

IP codes: *D*, dilute solution; *L*, low concentration; *I*, intermediate concentration; *F*, filtration; *FW*, filtration and washing; *RL*, residual liquid; *C*, concentrated solution; *S*, semi-carbonized product.

● Series 1: Since dilute H₃PO₄ catalyzes the hydrolysis of hemicelluloses, this series of IPs was prepared by further diluting D and by effecting the FIT and SIT only once with the starting D (16 g/100mL) and with two more diluted H₃PO₄ solutions, namely 5.33 g/100mL (DL1) and 10.66 g/100mL (DI1). Using the most diluted solution (i.e. that used in the preparation of DL1), the impregnation process was also carried out successively twice or three times with identical aliquots (DL2, DL3). In this way, the eventual amount of H₃PO₄ used in the various impregnation treatments was the same for DL2 and DI1 and for DL3 and D. Accordingly, not only CS but also previously H₃PO₄-impregnated CS were used in the impregnation treatments.

● Series 2 was also prepared with D. However, unlike in the preparation of series 1, after the FIT the supernatant liquid was filtered (DF), the residual solid was thoroughly washed with distilled water (DFW) or the filtrate was used as the impregnation solution for a fresh sample of CS (DRL). The preparation of DRL was intended not only as a different impregnation strategy concerning the dilution of H_3PO_4 but also to obtain information on the feasibility of recycling.

● For Series 3, C was oven-dried at 120 °C for 2-24 h before its use in the FIT of CS. This impregnation strategy was devised by taking into account the possible dependence on the concentration of the physical and chemical state of H_3PO_4 in the impregnation solution.

● Regarding Series 4, CS were first heat-treated at 200 or 300 °C for 2 h in N_2 (flow = 100 mL/min) and the resulting chars (semi-carbonized CS), which are designated S200 and S300, were then impregnated with D and C. This strategy concerned the influence of composition of the lignocellulosic substratum on impregnation. The impregnation methods are summarized in Table 3, which also includes mass data and sample codes. To the authors' knowledge, this is the first time such methods are used in the impregnation of lignocellulosic materials with H_3PO_4 . As a guide, see references (Molina-Sabio et al. 1995; Stamm 1934) for comparison purposes.

3. Results and discussion

3.1. Mass changes

The mass increase produced by impregnation of CS and CS chars with H_3PO_4 solution was calculated through Expression (1)

$$\Delta m = m_f - m_0 \quad (1)$$

where m_0 and m_f are the initial and final mass of sample, and Δm the mass of H_3PO_4 loaded into the CS. Therefore, m_f represents the neat mass change associated not only with the loading of activating agent on CS and CS chars but also with physical and chemical processes which likely occurred during the impregnation process (i.e. solubilisation, hydrolysis, other chemical reactions, and so on) with involvement of the lignocellulosic material (Baquero et al. 2003; Lim et al. 2010). The aforesaid processes only caused mass decrease that influenced m_f provided that the resulting products, because of their volatility, were released from the medium during any of the impregnation treatments. The obtained Δm values have previously been reported (González-Domínguez et al. 2011, 2017) and are collected in Table 3. In brief, it was shown that Δm :

- Markedly decreases with the dilution of the dilute solution (IPs DL1, DI1 and D).
- Significantly decreases when the impregnation process was effected more than once with aliquots (IPs DL1, DL2 and DL3). As a guide, for D0 and DL3 (i.e. both IPs prepared using the same amount of H_3PO_4), the percentage of H_3PO_4 loading is 45.6 and 33.4 (as obtained from $\Sigma\Delta m$), respectively.
- Greatly decreases for the IPs prepared by removing the filtrate and by further washing the resulting product with distilled water. Δm is approximately five- and fifteen-fold for D0 that for DF and DFW, respectively.
- Noticeably increases for DRL. For this IP Δm is 10.9 g, which is therefore pronouncedly higher than 7.3 g for D0. By taking 1.34 g as the amount of H_3PO_4 loaded on CS in the FIT (i.e. the same as in the preparation of DF), the surplus of substance remaining in the filtrate was 14.66 g. Then, it follows that Δm was higher when the filtrate was used as the impregnation solution, in spite of the fact that the presence of H_3PO_4 in the filtrate was smaller than in D (i.e. 14.66 g as compared to 16 g).

● Increases with the concentration of the impregnation solution, as seen above, but especially when C was used. The percentage of H_3PO_4 loading is as high as 93.8 for C0 whereas for D it is 45.6.

● Varies rather irregularly with time of the previous oven-drying of C at 120 °C. Clearly, loading was only significantly promoted when oven-drying for the shortest time of 2 h. For longer times, as compared to C0 (i.e. the IP prepared without prior oven-drying), it first significantly decreases and then remains almost unchanged.

● Is also strongly dependent on whether CS or CS chars were used as the substratum in the impregnation with H_3PO_4 . Δm is higher for the CS chars, in particular for S300, than for CS, provided that D was used. For C, however, Δm is slightly lower for S200C than for C0. In the case of S300C, drying was not completely achieved after the SIT and therefore, Δm could not be obtained (González-Domínguez et al. 2011).

3.2. Insights into the impregnation mechanisms

3.2.1. Impregnation with dilute H_3PO_4 solution- by further dilution

The obtained values of Δm for DL1, DI1 and D0 (Table 3) point out a noticeably increased reluctance of H_3PO_4 to its loading on CS with the successive dilution of the impregnation solution. As a tentative, it may be accounted for by thoroughly examining the effects on the composition of the solution associated with the impregnation process throughout which CS swelling and shrinkage occurred, as follows. The CS constituent biopolymers (cellulose, hemicellulose and lignin) contain oxygen functional groups which are hydrophilic in nature and may attract water molecules through hydrogen bonding, although some groups such as glycosidic bridges and ethers may not have this high capability. Anyways, the material should start swelling in a single phase uniform

(homogeneous) system such as the H_3PO_4 solution as soon as contact was established between the solid/liquid phases in the FIT. Certainly, such oxygen groups should be necessarily accessible to water as swelling occurs. In this connection, it is pertinent to note that lignocellulosic materials are inherently recalcitrant to chemicals and enzymes due to a wide series of natural factors (Himmel et al. 2007). Further, a characteristic of the swelling process is the anisotropy. For lignocellulosic materials such as woods, swelling varies by tangential (i.e. in the direction of the annual growth rings)>> radial >> longitudinal (Stamm 1964). Other factors with influence on the swelling process are related to the composition, solvent, and heat treatment temperature. The various biopolymers of lignocellulosic materials participate unevenly in the swelling process. Thus, hemicelluloses are the most hygroscopic polymer in cell walls, followed by lignin and finally cellulose, in particular crystalline cellulose (Himmel et al. 2007). Swelling is significantly enhanced by the removal of extractives by the action of solvents (Mantanis et al. 1994). Solvents such as water with a great ability to bind by strong hydrogen bonding possess a large swelling capacity (Mantanis et al. 1994; Stamm 1964), the process being then very favourable. This process is extremely fast even at room temperature and significantly increases its rate at higher temperatures. At 100 °C, the rate of swelling tremendously increases. However, the maximum swelling only increases slightly as the temperature increases. As a result of swelling, the material expands until the cell wall becomes saturated with water (fiber saturation point) (Stamm 1964). For all wood species, this point is reached for the moisture content of approximately 30% (1957). Moisture beyond the fiber saturation point is free water and does not contribute to further expansion (Mantanis et al. 1994).

Insofar as CS swelled and expanded, the diffusion of H_3PO_4 in CS would be easier and this should enable the H_3PO_4 molecule to compete with the water molecule

for oxygen functional groups of CS biopolymers to bind by hydrogen bonding. In fact, the hydrogen bonding potential of the H_3PO_4 molecule is even larger than for the water molecule. In crystalline state, each H_3PO_4 molecule is linked to six others by hydrogen bonds and extensive hydrogen bonding persists on fusion (Greenwood and Earnshaw 1989). In aqueous solution, such a potential may be even more effective than for other aggregation states of matter on account of the absence of steric hindrance to bind to water molecules. Nevertheless, competition should be unfavorable for H_3PO_4 because of the lower polarity of the O-H bond for H_3PO_4 . Dissociated H_3PO_4 should be able to form stronger hydrogen bonding than the neutral molecule, owing to the involvement of the negatively charged H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} ions. However, H_3PO_4 in aqueous solution is poorly dissociated and to a lesser degree when heating above room temperature. Since the FIT was performed at 85 °C, the thermal agitation of the system is another factor that should also handicap the involvement of the H_3PO_4 molecule in hydrogen bonding in the bulk of the solution and with oxygen groups of CS. The effect would be weaker than for the water molecule which binds more strongly by hydrogen bonding than the H_3PO_4 molecule. In any event, it should be noted here that even in the case of water in the liquid state, the fluctuating molecular aggregates are continuously changing by effect of the thermal agitation on hydrogen bonding (Doménech 1998). In brief, the extensive hydrogen bonding of H_3PO_4 in the bulk of the solution and its weaker hydrogen bonding to oxygen groups of CS as compared to water together with the thermal agitation of the system would contribute to stabilize H_3PO_4 in the bulk of solution rather than in the loaded state, this rendering the loading process of H_3PO_4 difficult in the FIT.

In the SIT, which was carried out by oven-heating at 120 °C for 24 h, the vaporization of water from the supernatant in contact with the lignocellulosic

substratum and also of indigenous water of CS (i.e. free water, linked water and water of constitution) occurred. Water rather than H_3PO_4 should preferably vaporize in accordance with the markedly lower boiling point of water than of H_3PO_4 . Concomitant with the process of water vaporization, H_3PO_4 should become progressively more concentrated in the transient liquid in contact with CS. However, simultaneous to its concentration, H_3PO_4 should be loaded on CS, this being then a tending factor to lower the concentration of H_3PO_4 in the aforesaid liquid. Thus, in brief, the processes of vaporization, concentration, and loading were time-dependent and interdependent with each other. As a result of vaporization and concentration, the boiling point increased and vapour pressure decreased with the course of time. That is to say, the tendency of the liquid to vaporize was progressively smaller with time. Furthermore, owing to its dependence on concentration, the boiling point was first below (i.e. $> 100\text{ }^\circ\text{C}$; as a guide, for 10 wt% H_3PO_4 solution is $100.2\text{ }^\circ\text{C}$ (Toy 1973) and then above $120\text{ }^\circ\text{C}$. Accordingly, the liquid first boiled and then evaporated. Since the mass of liquid taking part in the vaporization process was different in both instances (i.e. the process occurred within the entire mass of the liquid and only on its surface, respectively), it should influence the degree of thermal agitation in the system and the kinetics of the vaporization process, which was first faster and then progressively slower. As a result, the aggregation of H_3PO_4 units by hydrogen bonding during the evaporation process would be promoted not only on account of the concentration rise but also, from a given oven-drying time on, because of a lesser agitation in the system. Aggregation should originate a stability gain against evaporation and for the loaded state as it should propitiate the loading of large size units which would be able to interact simultaneously with a larger number of active sites of the lignocellulosic substratum.

Another factor that likely contributed to stabilize H_3PO_4 in the loaded state was the shrinkage undergone by the swollen CS in the SIT. Swelling is a reversible process and a given material shrinks as it loses moisture (Mantanis et al. 1994). Shrinking occurs only at moisture content values below the above-mentioned fiber-saturation point. Furthermore, shrinkage is proportional to the amount of moisture lost below such a point (1954). Therefore, shrinkage only commenced after a great proportion of moisture had been removed from the swollen CS by evaporation. Of course, water should have also been vaporized before from the bulk of the transient liquid. Regarding H_3PO_4 , since the un-evaporated amount of it still remaining in the system was too small (i.e. much more than that of CS) to form a two-dimensional liquid on the surface of CS, it should be found therefore up-taken in CS. On going on oven-heating, H_3PO_4 to some extent might also be removed from CS, although the process should be less favourable than for water as the vapour pressure is lower for H_3PO_4 . Besides, a greater availability of active sites by moisture loss would enable H_3PO_4 to further bind to CS. Further, the volume contraction should hinder the release of H_3PO_4 from CS, particularly with the increase in the degree of H_3PO_4 aggregation in the up-taken state. The presence of H_3PO_4 in CS may diminish its shrinkage, similarly to for inorganic salts (Stamm 1934).

From the above statements it follows that the aggregation of H_3PO_4 would have been a key factor with regard to its stabilization against evaporation from the transient impregnating liquid and, after its loading on CS, from the up-taken state and therefore to its eventual neat loading on CS during the SIT long. However, since the impregnation of CS was effected with dilute H_3PO_4 solutions, it is likely that aggregation was significantly restricted by an insufficient presence of H_3PO_4 . In addition, the thermal agitation of the system was opposed to aggregation. These two factors, in particular the former, should play a decisive role on H_3PO_4 , which would tend to evaporate instead of

becoming loaded on CS, which would be in line with the observed variation of Σm with the degree of dilution of the impregnation solution. In short, depending on whether the concentration of the initial H_3PO_4 solution was lower or higher the process of either vaporization or loading was more dominant in the SIT.

3.2.2. *Impregnation with dilute H_3PO_4 solution - step-by-step*

The significantly smaller loading of H_3PO_4 when the impregnation process was effected by successively repeating it (DL1, DL2, DL3) as compared to the single impregnation process strategy (DL1, DI1, D0) indicates that the H_3PO_4 -impregnated product resulting from a previous impregnation process (consisting of both soaking and drying steps) became passivated to its further impregnation with a fresh aliquot. This is ascribable to changes produced in the chemical composition of CS as a result of the previous impregnation process, namely the lixiviation of soluble fractions and the hydrogen bonding between H_3PO_4 and polar oxygen species in CS. Such a composition should mainly be affected during the SIT as H_3PO_4 concentrated in the transient liquid in contact with CS, and as a result, its reactivity against CS structural biopolymers should increase, as evidenced by previously reported results. Thus, hemicelluloses are readily soluble in water (Horvath 2006). Extractives are also removed by the action of a polar solvent such as cold and hot water (Vassilev et al. 2012). From the chemical standpoint, H_3PO_4 may act as a reactant or as a catalyst. As is well known, the H_3PO_4 molecule may condensate with one or more surface hydroxyl groups of metal oxides giving one or more water molecules. Dilute H_3PO_4 at moderate temperature (i.e. typically 1-10 wt.% and 100-150 °C; Lenihan et al. 2011) catalyzes the hydrolysis of the hemicellulose fraction. However, it does not attack the cellulosic fraction to an appreciable extent (Gámez et al. 2006).

3.2.3. Impregnation with dilute H_3PO_4 solution - by filtering and washing

From the very high sensitivity of the loading of H_3PO_4 on CS to the removal of the supernatant liquid after the FIT of CS with the dilute H_3PO_4 solution and to the washing of the residual product with distilled water, it is evident in turn not only that the activating agent was scarcely prone to become loaded on the lignocellulosic substratum in such a step of the impregnation process but also that the fraction of H_3PO_4 that achieved it to a large extent was susceptible to be removed from the previously loaded state by the washing action of water. From these results, it is evident that the interaction of the substratum with H_3PO_4 was weak and that loading was then a reversible process. On the other hand, these results prove that in the impregnation process most loading of activating agent occurred during the SIT. It is likely that, after this impregnation step, organic matter leached out before from CS by physico-chemical action of the dilute H_3PO_4 solution (i.e. mostly hemicelluloses and extractives) was found either dissolved in the residual liquid or simply deposited on CS, being then easily removed during the filtration and washing operations and thus, also causing mass decrease.

3.2.4. Impregnation with dilute H_3PO_4 solution - using the filtrate as an impregnating solution

The enhanced mass increase produced when the impregnation of CS was performed using the filtrate obtained after the FIT as the impregnation solution was at first surprising. Because of the presence in such a liquid of not only H_3PO_4 remaining in excess after the previous FIT of a CS specimen but also of organic matter coming from CS, it was expected that the effects of the impregnation solution (i.e. filtrate) on biopolymers of a fresh CS specimen, due to processes of hydrolysis, catalysis, and so

on, would have been mitigated. However, when studying the hydrolysis of sugar cane bagasse (SCB) using H_3PO_4 at the ratios of H_3PO_4 to SCB of 2, 4 and 6 % and heating at 122 °C for 0-300 min (i.e. the reactant ratios are much lower and the treatment times are much shorter than for the present study), it was found by Gámez et al. (2006) that the solubilised fraction (SF) is a function of both the H_3PO_4 /SCB ratio and treatment time. Thus, SF as a rule increases as both variables of the hydrolysis process increase. However, for high reactant ratios and long treatment times SF markedly decreases. From these results it becomes apparent that a stronger solubilisation effect at shorter times to a great extent inhibits the process at longer times. It was also stated by the same authors that in the operation of concentration of the hydrolysates by evaporation, besides water, small amounts of growth inhibitors such as acetic acid, furfural and hydroxymethylfurfural are removed (Gámez et al. 2006; Martínez et al. 2002 and citations therein). Accordingly, it seems that to the mass increase produced when the filtrate was used as the impregnation solution contributes the loading of not only H_3PO_4 but also of organic matter. The organic fraction may make up of products arising from physico-chemical interactions of H_2O and H_3PO_4 with CS biopolymers in both FITs and in the SIT which did not undergo evaporation during the SIT and that remained loaded, perhaps simply deposited, on CS after the SIT.

3.2.5. *Impregnation with concentrated H_3PO_4 solution – using commercial H_3PO_4*

From the very high Δm obtained for C0 (i.e. the mass loss was as low as 20 wt.% and it should be further taken into account the probable loss of indigenous water of CS during the SIT) than for D0 it is evident the high tendency exhibited by H_3PO_4 to the loading on CS, as an opposing effect to its removal by evaporation, during the impregnation process, which consisted of the FIT and SIT.

In the FIT, it is likely that the swelling of CS in the H_3PO_4 solution was a very important factor in connection with the loading process of H_3PO_4 . Swelling was accompanied by an increase in the pore size and accessible surface area of CS (Stone et al. 1969), which should facilitate the diffusion of H_3PO_4 in CS and enhance the uptake of H_3PO_4 . Using cotton linters and 72.0 to 78.8% H_3PO_4 solutions at 2 °C, it was observed earlier that they were swollen to an increasing extent with increasing concentration of the acid solution. The swelling increase was especially sensitive only for the most concentrated acid solutions. As a result of swelling, the surface area of the cellulose gel was accessible to a molecule of 40 Å diameter (Stone et al. 1969). On the basis of the higher concentration of the H_3PO_4 solution used in the impregnation of CS (85 wt.% instead of 78.8 wt.% at most) and of the higher temperature of the swelling system (i.e. 85 °C instead of 25°C), it may be speculated that the degree of swelling of CS in such a solution was large, and that the swollen material was then internally accessible even to large size molecular aggregates of H_3PO_4 present in the solution. After swelling, H_3PO_4 should interact physico-chemically with chemical constituents of CS. In relation to mass balance, the changes produced in the basic structural components of CS are of particular relevance in the present study.

Because of its fibrous structure and the strong hydrogen bonds, cellulose is insoluble in most solvents (Horvath 2006), including water and most common organic liquids (Swatloski et al. 2002). However, it can be directly dissolved in concentrated acids, for example, H_3PO_4 , which possess higher reactivity toward hydrogen bonds than the dilute acids (Harris and Lang 1947) and that disrupt such bonds in the cellulose chain and convert it to an amorphous state. The de-crystallized cellulose forms a homogeneous gel without the acid, which allows hydrolysis reactions (Orozco et al. 2007). The dissolution of cellulose leads to hydrolytic cleavage of its chains, and the cellulose

molecules are transformed to derivatives, such as esters (Horvath 2006). The interaction of mineral acids with polysaccharides proceeds via protonation of the oxygen atom on glycosidic bonds, stabilization of the pyranosyl cation by mesomerism, formation of oxonium ions by water addition, and stabilization of it by hydrogen splitting (Dobele et al. 2003 and references therein).

Regarding lignin, this biopolymer has a very low solubility in most solvents. If a solvent dissolves cellulose, then it is more likely that it also dissolves hemicelluloses and lignin. If lignin is bonded to carbohydrates, it requires chemical degradation for solution (Horvath 2006). Thus, there is no known method for isolating unaltered lignin from plant cell walls, and chemical (or biochemical) degradation methods produce low molecular weight products in modest yields only (Kilpelainen et al. 2007). Nevertheless, Fierro et al. (2005) pointed out that the reaction of kraft lignin with 85 wt.% H_3PO_4 aqueous solution starts at room temperature as soon as they are mixed since the temperature of the sample increases immediately. This observation was in agreement with Lai (1991) who reported that cleavage of aryl ether bonds is accompanied by dehydration, degradation and condensation reactions together with formation of ketones by hydrolysis of ether linkages at low temperatures. According to Jagtoyen and Derbyshire (1998), the reaction of wood with 28 wt.% H_3PO_4 solution probably begins at temperatures as low as 50-100 °C first with the attack of hemicellulose and lignin. Loss of carboxyl and methyl groups from hemicelluloses even at 50 °C and changes in lignin composition occurred.

In the light of the above statements it is clear that under the soaking conditions of CS with the concentrated H_3PO_4 solution not only hemicelluloses (and extractives), as described above, but also cellulose and lignin were susceptible to interact physico-chemically with H_3PO_4 . Probably, the action of this acid during the FIT was controlled

by the accessibility of the CS biopolymers, which will depend on factors such as the swelling process and chemical structure of CS. In the first place, it is worth underlining again here that a characteristic of the swelling of lignocellulosic materials is its anisotropy, which is important as the degree of swelling should determine the internal surface area of contact between the solid and liquid phases. Furthermore, composition changes produced as a result of such a process would further increase the accessible porosity. This was associated with the removal of hemicelluloses by Grethlein (1985). However, it was also stated that the attack first of the hemicellulose and lignin by H_3PO_4 was due to an easier access to these biopolymers than to the crystalline cellulose (Jagtøyen and Derbyshire 1998). Therefore, the acid treatment to some extent may strip hemicelluloses and lignin. For cellulose, ordered regions and highly disordered regions exist alternatively in its fibrils (Ho et al. 2011). A limited swelling of the amorphous cellulose (i.e. dependent on the hydrogen bonding strength and molecular size of the solvent) would not cause intercrystalline swelling (Horvath 2006). Neither water nor other small molecules can penetrate the very tight crystallites. Out of the main biopolymers of lignocellulosic materials, cellulose is therefore the most recalcitrant one.

In the SIT, an important factor related to the thermal stabilization and loading process of H_3PO_4 was likely the degree of association of H_3PO_4 in the transient impregnating liquid before its loading on CS. As compared to the initial concentrated solution, a further aggregation of H_3PO_4 in the aforesaid liquid was possible, provided that the kinetics of the evaporation process for water was faster than that of the loading process for H_3PO_4 as it should result in a concentration increase. Because of the influence of concentration on physical properties such as viscosity, boiling point, and vapour pressure, it would enable smaller H_3PO_4 aggregates to become closer and to interact slower by cohesive forces. Eventually, a viscous syrupy liquid may be formed

as the amount of H_3PO_4 contained in the impregnation solution (i.e. 144.5 g in 100 mL of solution) was much larger than that of CS (i.e. 25 g). Since CS can be regarded as a high energy solid, as the bonds between atoms of its constituent chemical elements are very strong, such a liquid should achieve complete wetting with its surface. Of course, adhesion should be strong and/or extensive enough so the loading process was feasible from the thermodynamic standpoint. Loading would prevent H_3PO_4 from evaporation, with the consequent mass increase of IPs. However, loading may be hindered as a result of textural changes produced in the material because of drying (i.e. hornification is the term used in the paper industry to describe such changes). Thus, when wood pulp was dried by various methods it was found by Esteghlalian et al. (2001) that it significantly reduced the population of larger pores and that the partial closure of larger pores created a larger number of smaller pores. These textural effects may render the diffusion of H_3PO_4 in CS porosity difficult and its evaporation from the liquid state easier than from the loaded state, which would become stabilized against evaporation.

After wetting, if H_3PO_4 were found in liquid state, it would dissolve cellulose, which may be hydrophobic or hydrophilic in nature. In fact, it was previously reported that anhydrous phosphoric acid (i.e. with a P_2O_5 concentration above 74%, superphosphoric acid) is an excellent direct solvent for cellulose (Boerstoeel et al. 2001). Furthermore, by treating the cell walls chemically, it is possible to isolate smaller or wider cellulose fibril aggregates. Since cellulose fibers are commonly negatively charged due to the presence of $-\text{O}^-$ and $-\text{COO}^-$ groups, which arise from deprotonation of alcohol and small amounts of carboxylic acid groups respectively (Ho et al. 2011), and H_3PO_4 in liquid state undergoes extensive self-ionization (Greenwood and Earnshaw 1989), the formation of sorts of ion pairs in the suspension would further contribute to stabilize the cellulose aggregates in the impregnation system. In addition, the

stabilization of lixiviated organic matter by hydrophobic interactions occurring either in the bulk of the suspension or with the remaining un-attacked fraction of the lignocellulosic substratum should not be ruled out. In this connection, it should be recalled here that hydrophobic compounds commonly possess a long hydrocarbon chain with little reactive functional groups or its ionic charge is screened. Finally, because a high molecular weight, aforesaid aggregates should have a low tendency to vaporize. In short, they should be prone to remain in the system after the SIT, contributing to the final mass of IP.

3.2.6. Impregnation with concentrated H_3PO_4 solution – using H_3PO_4 after oven-drying

When the concentrated H_3PO_4 solution was oven-dried for 2-24 h prior to the use in the impregnation process of CS, the variation of Δm was noticeably irregular and sometimes more significant (see data in Table 3). After oven-drying such a solution itself, it was observed that its volume reduction was strongly time-dependent. It was practically inappreciable for 2 and 24 h and approximately 10 vol.% for 12 h (instead of as low as 10 vol.% at most, as previously erroneously reported; González-Domínguez et al. 2011). Although it was expected that the volume reduction was slight because of the high concentration of the H_3PO_4 solution (i.e. the content of P_2O_5 in a 85 wt.% H_3PO_4 solution is 61.55 wt.%; Toy 1973), it is exceedingly smaller in some instances, as for the heating time of 24 h. Since the 85 wt.% solution H_3PO_4 must contain the dimeric species $(H_3PO_4)_2$ (i.e. two acid molecules associated via hydrogen bonding) (Wertz and Cook 1985), the degree of H_3PO_4 aggregation and the loss of water by evaporation should increase with heat treatment time. During the FIT of CS with the resulting H_3PO_4 concentrated solutions, the stirring of the heterogeneous mixture became more

difficult. Furthermore, solidification occurred practically at the end of the FIT for C12 and the formation of a solid phase on the surface of a very viscous liquid was easily visible for C24. After the SIT of the residual heterogeneous mixture, which was made up of a solid and a more or less viscous liquid, a sponge-like compact mass was obtained, the appearance of which being quite different from that of Series 1 and 2 IPs. From these observations it is clear that the previous oven-drying of the H_3PO_4 solution markedly influenced the physical properties of the liquid in contact with CS during the SIT. As compared to the impregnation treatment with the non oven-dried solution, it was expected that as a result of water vaporization during the previous heating a more concentrated solution of H_3PO_4 was longer in contact with the substrate during the SIT and that this would influence the degree of H_3PO_4 aggregation and the size of the aggregates loaded on CS. The occurrence of changes in the chemical composition of H_3PO_4 should not be ruled out on account of the concentration increase. Nevertheless, in this connection it should be borne in mind, however, that impregnation was carried out by heating at 85 and 120 °C in the successive steps of the impregnation process and that the formation of the dimer $\text{H}_4\text{P}_2\text{O}_7$ by condensation reactions involving H_3PO_4 occurs at temperatures as high as 213 °C (Platanov 2000) and 240 °C (Sharpe 1989).

3.2.7. Using CS chars as the feedstock

The Δm increase for S200D and for S300D (i.e. both IPs prepared with the dilute H_3PO_4 solution) is ascribable to porosity development in CS as a result of the charring process as it should favour the diffusion of the impregnation solution in the chars and hence, the loading of H_3PO_4 . Porosity was created due to the loss mainly of water at 200 °C and of water and hemicelluloses at 300 °C (Liu et al. 2011; Yang et al. 2007). Therefore, the thermal effect on the texture of CS embraced the entire mass of CS. In

this respect, it was different from that of swelling as this process is characterized by its anisotropy. In accordance with the Δm values, the textural effect on the loading of H_3PO_4 was markedly stronger for S300D than for S200D, as expected, since the mass loss produced by dehydration and partial devolatilization of CS was higher when charring at 300 °C. In addition, the size of chemical species removed from CS was different at both charring temperatures, which should influence the porosity distribution and accessibility in the charred products and as a last resort the loading process.

S200C and S300C were prepared with the commercial concentrated H_3PO_4 solution. For S200C, as compared to C0, the Δm values indicate that loading slightly decreased. In the case of S300C, however, a certain amount of readily visible liquid remained after oven-drying at 120 °C for 24 h in the SIT. Such a liquid was separated by filtration and the residual impregnated product was oven-dried again. Clearly, these results advocate for a restricted diffusion of H_3PO_4 in the chars. Likely, it was due to the presence of narrow pores in the chars and of large H_3PO_4 molecular aggregates in the impregnation solution. The size of the pores would be determined not only by the size of the matter affected by dehydration and devolatilization processes of CS and by its distribution in the bulk of the mass of CS but also by another concurrent thermal effect of mass contraction. This would be responsible for a further porosity shrinkage which rendered its access more difficult. Surely, it also decreased the degree of swelling of the chars in the impregnation solution and as a last resort the loading of H_3PO_4 . In part, loading should be mechanical instead of by a physical or chemical process. On the other hand, the stronger unfavourable effect for S300 is attributable to a more limited swelling of this char than of S200 in the impregnation solution. It should prevent H_3PO_4 from accessing biopolymers still remaining in the char and thereby from becoming stabilized in the loaded state. Despite this, H_3PO_4 remained in the system saturating the char, as

expected. Thus, 120 °C is a temperature well below the boiling point of H₃PO₄ (Brown and Whitt 1952) and at this temperature, H₃PO₄ possesses a low vapour pressure, and therefore, it must evaporate slowly.

3.3. Implications in the AC development and composition

By subjecting to thermal treatment to all the aforesaid IPs (at 500°C for 2h), a wide range of activated carbons can be prepared (González-Domínguez et al. 2017). As seen in Table 4 and Figure 4, high concentrations of the H₃PO₄ activating agent usually produce high specific surface areas (~ 1500 m² g⁻¹), while lower H₃PO₄ amounts create narrower pores and more homogeneous pore size distributions. The efficiency of the activation process can be improved through the control of the thoroughly described impregnation variables:

Table 4: Surface characterization of the AC derived from the IPs described in the present work. B.E.T. surface area (González-Domínguez et al. 2017) and chemical surface composition obtained by XPS.

AC sample	S _{BET} (m ² /g)	Surface at. %			
		%C	%N	%O	%P
DA	640	80.5	2.0	15.2	2.0
DL1A	123	84.9	1.4	11.4	2.3
DL2A	512	86.1	0.5	10.9	2.5
DI1A	351	82.3	1.1	13.9	2.8
DL3A	837	82.6	1.7	13.1	2.6
DFA	134	84.5	1.5	11.9	2.2
DFWA	337	87.3	2.3	10.4	~ 0
DRLA	791	82.8	1.9	12.9	2.3

C0A	1491	91.2	~ 0	6.7	2.1
C2A	1203	88.2	~ 0	8.8	2.9
C6A	1441	90.1	~ 0	7.6	2.3
C12A	1440	90.8	~ 0	7.0	2.2
C24A	1438	87.3	~ 0	9.8	2.9
S200DA	660	85.8	~ 0	11.6	2.6
S300DA	330	82.7	1.2	12.4	2.9
S200CA	1489	85.7	~ 0	10.8	3.5
S300CA	596	75.1	0.9	17.7	2.9

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- 645 • Number of impregnation steps: porosity development increases when the
646 impregnation is performed in several steps with dilute solutions, instead of only one
647 impregnation with an identical amount of H_3PO_4 . Similarly, super-concentrating the
648 commercial H_3PO_4 solution does not lead to further increases in the porosity.
- 649 • Reutilization of the H_3PO_4 solution: two activated carbons (337 and $791 \text{ m}^2 \text{ g}^{-1}$) can
650 be prepared with the same H_3PO_4 amount that is needed for the preparation of only
651 one adsorbent ($640 \text{ m}^2 \text{ g}^{-1}$) by direct impregnation.
- 652 • From activation experiments starting with semi-carbonized CS, it has been
653 recognized that biopolymer components decomposed at 300°C play a key role in the
654 activation mechanism with H_3PO_4 .
- 655 • As regards the surface chemical composition, the series of AC which underwent
656 impregnation with diluted H_3PO_4 solutions present a C/O ratio in the range of 5 – 8,
657 while concentrated impregnation solutions give rise to a C/O ratio in the range of 10
658 – 14. Nitrogen contents also differ significantly from one case to the other, being

almost inexistent for ACs impregnated with concentrated H_3PO_4 solutions.

Surprisingly, the phosphorus content seems to be practically unaltered in all cases.

Further, the effect of semi-carbonization is also visible.

The operational strategies studied in this work can be applied to the efficient preparation of activated carbons with tailored porosities and surface chemistries for specific applications, according to the underlying chemical processes occurring between H_3PO_4 and biomass.

Fig. 4. Compendium of pore volumes of the different AC samples obtained after carbonization of the IPs described in the present paper. $V_{0(N_2)}$ = micropores by nitrogen adsorption; V_{me} = mesopores by mercury porosimetry; V_{ma} = macropores by mercury porosimetry. (González-Domínguez et al. 2017).

4. Conclusion

A wide series of non-conventional strategies was used in the impregnation of CS with H_3PO_4 in aqueous solution (González-Domínguez et al. 2011, 2017). In this technical report, the results previously collected from such experiments are

comprehensively discussed and linked to essential chemistry knowledge, eventually drawing potentially interesting information. The mass changes were evaluated and tentatively accounted for, in general, by considering them dependent on the concentration of the H_3PO_4 solution and its chemical and physical properties, their evolution along the impregnation process and influence on the degree of association and loading of H_3PO_4 , in connection with the biopolymer composition of the lignocellulosic substratum and with its wetting, swelling and/or shrinkage. Valuable information is inferred with a view to setting up experimental methods that may pave the way towards a controlled interaction of H_3PO_4 with the feedstock and as a last resort preparation of activated carbon with tailored textural properties to be used with specific ends. In summary, by using dilute H_3PO_4 solutions in the impregnation stage, one can obtain a higher porosity development in ACs by successive steps with lower H_3PO_4 concentration, rather than in a single step with a more concentrated acid. The reutilization of H_3PO_4 is feasible, and provides a means to fabricate ACs with lower reagents consumption and good properties. Finally, the use of concentrated H_3PO_4 solutions or CS chars as the feedstock can be advantageous for obtaining ACs with high porosity.

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