Development of activated carbon from vine shoots by physical and chemical activation methods. Some insight into activation mechanisms

M. Ruiz-Fernández · M. Alexandre-Franco · C. Fernández-González · V. Gómez-Serrano

Abstract Activated carbons (ACs) are prepared from vine shoots (VS) by the method of physical activation in air, CO_2 and steam atmospheres and by the method of chemical activation with H_3PO_4, $ZnCl_2$ and KOH aqueous solutions. The ACs were characterized texturally by N_2 adsorption at $-196\,°C$, mercury porosimetry, and density measurements. The method of chemical activation has been proved to be more effective than the method of physical activation to prepare ACs with a well-developed porosity. ACs with high micro- and mesopore volumes are prepared with $ZnCl_2$ and H_3PO_4. Using $ZnCl_2$, the volume of micropores is $0.62\ cm^3\,g^{-1}$ and the volume of mesopores is $0.81\ cm^3\,g^{-1}$. A greater development of macroporosity is obtained by KOH activation. The volume of macropores is as high as $1.13\ cm^3\,g^{-1}$ for the resulting AC. Yield of the process of preparation of the ACs is low for the method of chemical activation. Some insights into the performance of the activating agents in the activation process are provided.

Keywords Vine shoots · Activated carbon · Textural characterization

1 Introduction

Activated carbon is a carbonaceous material characterized by its porous structure and surface chemistry. These properties of AC depend on the starting material and method used

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in its preparation, including the activating agent and operational conditions, and thereby current research on this topic is aimed at testing new AC precursors and at setting up new methods of preparation or at improving the already existing ones. Amongst the materials more widely used in the large-scale production of AC are woods, coals, lignite, coconut shell, peat, fruit stones, and others (Bansal et al. 1988; Jankowska et al. 1991; Rodríguez-Reinoso 1997; Marsh and Rodríguez-Reinoso 2006; Bandosz 2006). At present, as a promising alternative, the use of industrial and agricultural waste products with such an end is being however investigated, with a view not only to their controlled removal and valorisation but also to obtain lower-cost ACs. This is an important issue since the use of AC may be restricted in some instances because of its relatively high production cost, in spite of being the preferred adsorbent (Rafatullah et al. 2010). As a consequence, a wide range of industrial (Mui et al. 2004; Rozada et al. 2005; Cardoso et al. 2008) and agricultural (Heschel and Klose 1995; Kannan and Sundaram 2001; Olivares-Marín et al. 2007) waste products have been tested as starting materials in the preparation of AC.

One such potential AC precursors is VS (Corcho-Corral et al. 2005, 2006; Valente Nabais et al. 2010). This waste is generated in most of the European Mediterranean countries as a result of conditioning works of the vineyards, carried out yearly by the farmers after harvesting the bunch of grapes. Spain abounds with vine shoots, the annual production being of several million tons (Jiménez Alcaide et al. 1992). In the Autonomous Community of Extremadura (Spain), such an amount was estimated to be 87,725 tons (Regional Government of Extremadura 2002; Melgar et al. 2003). Although virgin VS may be used as a domestic fuel, its Higher Heating Value (HHV) being 15.8 or 16.6 MJ kg^{-1} (Gañán et al. 2006), this VS application is mainly handi-

capped by a low density and hence high transportation cost and as a result VS are usually burnt in the open air with release of greenhouse gases. The use of VS for paper production (Jiménez Alcaide et al. 1992; Jiménez et al. 2004; Angulo Sánchez and García Romero 2005), extraction of polyphenols (Luque-Rodríguez et al. 2006), and organic substrate production has also been studied in past years (Pardo et al. 2007).

Activated carbon is commonly prepared by the well-known methods of physical activation and chemical activation. Here, using VS, AC is developed by both such methods, the influence of the activating agent on the porous structure being studied. ACs are prepared in air, CO_2 or steam and with H_3PO_4, $ZnCl_2$ and KOH aqueous solutions and the resulting products are characterized texturally by N_2 adsorption at $-196\,°C$, mercury porosimetry, and density measurements. Some respects of the performance of the activating agents related to the activation mechanism are also the object of a special attention.

2 Experimental

2.1 Starting material and reactants

The VS used in the present study were kindly furnished in a vineyard grown in the wine-producing region named Tierra de Barros (Badajoz province, Spain). As received, VS were air-dried, size-reduced and sized, the fraction of particle sizes lower than 1 mm being chosen for the subsequent preparation of the ACs. The ACs were compared with a commercial AC (Merck, 1.5 mm; ACM). All chemical were grade reagents: $ZnCl_2$ (97%, Panreac), H_3PO_4 (85%, 1.69 g/mL; Panreac), and KOH (85%, Panreac).

2.2 Preparation of the ACs

2.2.1 Method of physical activation

The carbonization of VS was carried out in a cylindrical stainless steel reactor, which was heated in a vertical electrical furnace (CHESA). The activation treatments in air and CO_2 were effected in a horizontal furnace, Carbolite (GHA 12/450). As an exception to the rule, the activation in steam was performed using a heating system (Iberlabo) made up of two- in series-closely interconnected horizontal furnaces, the first one operating at $250\,°C$ for water vaporization and the second one for the activation of the carbonized product. Using a peristaltic pump, a selected water flow was continuously propelled towards the vaporization furnace and steam was carried by a N_2 stream to the activation furnace. The carbonization and activation heat treatments were conducted by heating a given amount of sample at $10\,°C\,min^{-1}$ from

room temperature to maximum heat treatment temperature (MHTT) in an inert atmosphere of N_2 or in the reactive atmosphere of air, CO_2 or steam-N_2. The heat treatment was extended at MHTT for a prefixed soaking time. After that, the system was allowed to cool down to room temperature in the N_2 atmosphere and the obtained products were weighed and stored in airtight plastic containers.

2.2.2 Method of chemical activation

A sample of VS was first added to 250 mL of an aqueous solution of $ZnCl_2$, H_3PO_4 or KOH and, under a steady mechanical stirring by action of a magnetic device, heated for a preset time. Next, the solid and liquid phases were separated physically by filtration and the resulting solid residue was oven-dried at $120\,°C$ overnight, weighed and stored until subsequent use. The carbonization of impregnated VS was carried out by heating at $10\,°C\,min^{-1}$ from room temperature to MHTT in N_2 atmosphere. After a certain residence time at MHTT, the system was cooled down to ambient temperature in the same N_2 atmosphere. The resulting products were thoroughly washed with HCl solutions and/or distilled water to remove the remaining activating agent. The acid solutions used were 5, 3 and 1 M or 0.5 M for the carbonized product prepared from $ZnCl_2$- or KOH-impregnated VS, respectively. The products obtained were oven-dried, weighed and stored in plastic containers. The specific conditions of preparation of the samples by the physical and chemical methods are summarized in Table 1, which also lists the yield values and sample codes. The yield of a given process was calculated as $m_f/m_i \times 100$, m_i and m_f being the initial mass of sample and m_f the mass of the final product. Finally, it should be mentioned that the heating conditions and impregnation ratios used in the preparation of ACs were chosen in accordance with the results obtained in previous exploratory experiments.

2.3 Textural characterization of the ACs

The textural characterization of the samples was accomplished by N_2 adsorption at $-196\,°C$, mercury porosimetry, and density measurements. The N_2 isotherms were determined in a Quantachrome Autosorb-1 semiautomatic equipment. After oven-drying at $120\,°C$ overnight, about 0.15 g of sample was weighed, placed in a glass holder, and outgassed in the adsorption equipment at $250\,°C$ for 12 h, at a pressure lower than 10^{-3} Torr, prior to effecting adsorption measurements. From the measured isotherms, the specific surface area of the samples was estimated by the Brunauer, Emmet, and Teller (BET) equation (Brunauer et al. 1938). The micropore volume was calculated by applying the Dubinin-Radushkevich equation (Dubinin 1975). Also, micro- and mesopore volumes were obtained from the volumes of N_2 adsorbed at $p/p^0 = 0.10$ and at $p/p^0 = 0.95$.

Table 1 Methods of preparation of the ACs

S	Atmosphere/AA	Flow (mL min^{-1})/ AA:VS IR	MHTT/°C	t/h	Yield/wt.%	Code
VS	N$_2$	80	600	2	25.9	C600
VS	N$_2$	80	900	2	25.2	C900
C600	Air	10	275	1	55.2	A
C900	CO$_2$	10	750	1	85.2	CD
C900	N$_2$-steam	80(N$_2$)	750	1	30.2	S
VS	ZnCl$_2$	5:1	85	7	244.4	ZC-PI
VS	H$_3$PO$_4$	5:1	85	2	196.4	PA-IP
VS	KOH	2.1	85	2	91.4	PH-IP
PA-IP	N$_2$		500	2	8.6	PA
ZC-IP	N$_2$		500	2	10.2	ZC
PH-IP	N$_2$		800	2	5.7	PH

Abbreviations: S, substratum; AA, activating agent; IR, impregnation ratio; t, isothermal time at MHTT (maximum heat treatment temperature)

A Quantachrome Autoscan mercury porosimeter was used in the experiments of mercury intrusion, using about 0.3 g of sample. Once known the mass of sample and its volume (i.e. this was obtained from data of the mass of mercury present in the sample holder, density of mercury at the working temperature, and calibration volume of the holder), the mercury density of the sample was calculated. The helium density was measured in a Quantachrome stereopycnometer, using between 2 and 3 g of sample.

3 Results and discussion

3.1 Starting material

Data of the proximate analysis of VS (wt.%) are: moisture, 8.3; volatile matter, 76.8; fixed carbon, 12.4; ashes, 2.5. Concerning the chemical composition of VS, significant differences were not observed in an earlier study on the production of cellulosic pulp from VS for four varieties of VS and two growing systems (Jiménez et al. 2004). As reported also by the same authors, the holocellulose content of VS (67.14) is lower than for other non-woody agricultural residues and raw materials (i.e. wheat straw, sunflower stalks, cotton stalks, rise straw, husks of sugar cane, esparto, flax, and reed) but similar to that of pine and higher than that of olive pruning. The lignin content of VS (20.27%) is similar to that of eucalyptus and the aforesaid non-woody materials.

3.2 Preparation of the ACs. Yields

The yield of the process of preparation of the ACs is strongly dependent not only on the activation method and stage but also on the activating agent, as expected. In Table 1 it is seen that the yield of the carbonization of VS is only slightly higher for C600 than for C900. It indicates that, from the

standpoint of the mass change, the pyrolysis of VS was almost complete at 600 °C. At higher temperatures, the slight decrease produced in the mass of sample was likely associated with the loss of a small amount of heteroatoms such as hydrogen, increasing the C/H atomic ratio in the resulting carbonized product and hence the degree of its aromatization. The yield values of 25–26 wt.% for VS are close to those obtained in previous studies for other lignocellulosic materials carbonized at 600 °C, i.e. 25.5 wt.% for sawdust from holmoak (Valenzuela Calahorro et al. 1986), 22.9 wt.% for sawdust from olive grove pruning (Valenzuela Calahorro et al. 1992), 25.4 wt.% for cherry stones (Gómez-Serrano et al. 1999), and so forth. For the activation stage, yield ranges widely between 85.2 wt.% for CD and 30.2 wt.% for S, which is important in relation to the effect of the activation treatment on the porous structure. Thus, as is well known, an increase in burn-off during the preparation of AC is usually accompanied with the creation of large size pores (meso- and macropores) to the detriment of micropores. The low yields obtained for the activations in air and in steam are worth mentioning as the treatments in these atmospheres were performed under relatively mild conditions (i.e. at 275 °C in air and 750 °C in steam for 1 h). When investigating the suitability of a large number of agricultural by-products for the manufacture of granular activated carbon by steam activation, it was reported that for the particle size used (1–2.5 mm) the optimum values of burn-off range between 60–40% and the most favourable activation temperature between 850 and 900 °C at a water vapour content of 35 vol.% in the activation gas (Heschel and Klose 1995). On the other hand, the yield of the impregnation process of VS is very high, in particular for ZnCl$_2$. By contrast, the yield of the carbonization process of the impregnated products is very low, ranging between 10.2 wt.% for ZC and 5.7 wt.% for PH. These yield values are much lower than those previously reported, for instance, for the H$_3$PO$_4$ activation of

Table 2 Textural parameters of the samples

Sample	S_{BET}[a]/ m^2 g^{-1}	W_0[a]/ cm^3 g^{-1}	V_{mi}[a]/ cm^3 g^{-1}	V_{me}[a]/ cm^3 g^{-1}	V_{me-p}[b]/ cm^3 g^{-1}	V_{ma-p}[b]/ cm^3 g^{-1}	ρ_{Hg}/ g cm^{-3}	ρ_{He}/ g cm^{-3}	V_T[c]/ cm^3 g^{-1}	$V_{T'}$[a]/ cm^3 g^{-1}
C600	34	0.010	0.011	0.02	0.07	0.54	0.78	1.65	0.68	0.62
C900	5	0.001	0.001	0.01	0.08	0.38	0.86	1.27	0.38	0.46
A	322	0.16	0.22	0.06	0.03	0.58	0.70	1.72	0.92	0.77
CD	293	0.14	0.14	0.05	0.07	0.41	0.84	1.76	0.62	0.62
S	572	0.26	0.29	0.13	0.17	0.69	0.61	2.04	1.14	1.12
PA	1363	0.48	0.53	0.69	0.69	0.47	0.52	1.86	1.39	1.64
ZC	1726	0.59	0.62	0.81	0.81	0.37	0.49	1.69	1.45	1.77
PH	791	0.37	0.40	0.13	0.07	1.13	0.45	2.36	1.80	1.57
ACM	805	0.47	0.39	0.11	0.16	0.20	0.76	2.08	0.84	0.83

[a]The N$_2$ adsorption isotherm: S_{BET}, BET surface area; W_0, micropore volume (Dubinin-Radushkevich equation); V_{mi}, micropore volume (V_{ad} at $p/p^0 = 0.10$, V_{ad} = volume adsorbed); V_{me}, mesopore volume (V_{ad} at $p/p^0 = 0.95 - V_{ad}$ at $p/p^0 = 0.10$). W_0, V_{mi} and V_{me} are expressed as liquid volumes

[b]Mercury porosimetry: V_{me-p}, mesopore volume; V_{ma-p}, macropore volume

[c]Density measurements: $V_T = 1/\rho_{Hg} - 1/\rho_{He}$; ρ_{Hg}, mercury density; ρ_{He}, helium density

[d] $V_{T'} = W_0 + V_{me-p} + V_{ma-p}$

peanut hulls (36–22%) (Girgis et al. 2002), China fir (50.3–31.6%) (Zuo et al. 2009), peach stones (44–33%) (Molina-Sabio et al. 1995), cherry stones (50–30%) (Olivares-Marín et al. 2007), etc.

In brief, from the above results it is evident that the products of VS carbonization are very sensitive substrata to interact with air and steam under the activation conditions in these atmospheres. It also applies to VS with H$_3$PO$_4$, ZnCl$_2$, and KOH both in aqueous solution and during the carbonization of the intermediate impregnated products. Such a high chemical activity may be related to the chemical composition of VS. In this connection it should be recalled here that the usual time period for the growth of VS is one year and that the lignin content is 20.27% for VS (Jiménez et al. 2004), whereas for woods it is commonly about 30 wt.% (Núñez 2008).

3.3 Textural characterization of the ACs

3.3.1 N$_2$ adsorption

The N$_2$ adsorption isotherms at −196 °C measured for C600, C900, and ACs have been plotted all together in Fig. 2 for comparison purposes. As can be seen, except for PA and ZC, the isotherms belong to type I isotherm of the Brunauer, Deming, Deming and Teller (BDDT) classification system (Brunauer et al. 1940). Accordingly, the carbonized products and ACs as a rule are essentially microporous solids. As a peculiar feature, for PH and S the adsorption of N$_2$ undergoes a slight increases at values of the relative pressure (p/p^0) higher than 0.9, which is indicative of the presence of mesopores in these ACs. The isotherms determined

for PA and ZC may be regarded as a composite isotherm of types I and IV isotherms (BDDT classification). For this couple of ACs, as compared to the remaining ACs, the adsorption of N$_2$ is markedly higher at low p/p^0 and greatly increases at higher p/p^0. In a wide p/p^0 range between approximately 0.3 and 0.7 a significantly greater slope of the isotherm is observed for ZC than for PA, whereas the opposite is true at higher p/p^0 values. From these adsorption behaviours it becomes apparent that PA and ZC possess much better developed micro- and mesoporous structures than the other ACs. Furthermore, in these porosity regions the pore size distribution is very wide for PA and ZC. Moreover, a fraction of narrower mesopores is greater in ZC and of wider mesopore in PA.

The values of S_{BET}, W_0, V_{mi} and V_{me} obtained for C600, C900 and ACs are listed in Table 2. Concerning the method of physical activation, it should be indicated first that the products of VS carbonization possess a very poor development of micro and mesoporosity. It is so in particular for C900, which suggests that at 900 °C pore shrinkage occurs, decreasing the porosity accessible to N$_2$ at −196 °C. A microporosity decrease at high heat treatment temperatures was reported elsewhere (Neely 1981; Pastor-Villegas et al. 1993; Gómez-Serrano et al. 1996) and connected with lateral growth and increase in planarity of layer planes (Masters and McEnaney 1984). Second, for the ACs S_{BET}, W_0 and V_{mi} vary by S > A > CD. Also, V_{me} is significantly higher for S than for A and CD. For this couple of AC, V_{me} is in fact very low (i.e. 0.06 and 0.05 cm^3 g^{-1}, respectively). Accordingly, steam is the most effective activating agent to create micro- and mesopores in the carbonized product. In

the case of air and mainly of CO_2, only a smaller volume of micropores is created. For PA, ZC and PH, the values of S_{BET}, W_0, V_{mi} and V_{me} are large. The variation sequence for the whole of textural parameters is ZC > PA > PH. For ZC, S_{BET} is equal to 1726 $m^2 g^{-1}$, V_{mi} to 0.62 $cm^3 g^{-1}$, and V_{me} to 0.81 $cm^3 g^{-1}$. Notice that, thought to a lesser extent, S_{BET}, W_0, V_{mi} and V_{me} are also high for PA. These results indicate that by the method of chemical activation AC with a large development of micro- and mesoporosity is prepared and that the beneficial effect on these porosity regions is stronger with $ZnCl_2$ and also with H_3PO_4. For comparison purposes of both activation methods, the percentage of S_{BET} increase has been estimated by the expression $\{(S_{BET\text{-}ZC} - S_{BET\text{-}S})/S_{BET\text{-}S}\} \times 100$ ($S_{BET\text{-}ZC}$ and $S_{BET\text{-}S}$ are the BET surface areas obtained for ZC and S), being equal to 202. Using the same expression for V_{mi} and V_{me}, the obtained percentages are 114 and 523. In view of these results it is clear that the improved effect of the chemical activation is much stronger on mesoporosity than on surface area and microporosity.

3.3.2 Mercury porosimetry

From the curves of mercury intrusion (Fig. 2), as far as mesoporosity is concerned, it follows that the results of mercury porosimetry agrees usually with those of N_2 adsorption at $-196\,°C$. Thus, mesoporosity is better developed for ZC and PA, in contrast to C600, C900, A, and CD. Also, notice the presence of a significant amount of mostly wide mesopores in S. In the region of macropores, the pore size distribution is similar for C600, C900 and most of the ACs. The variation of the cumulative pore volume with pore radius indicates that macroporosity is heterogeneous in the aforesaid carbonaceous materials. This also holds for ZC. However, the content of macropores with a different size is markedly lower for ZC than for the rest of the ACs. The AC with the best developed macroporosity is PH. In the case of this AC, the macropore size distribution is narrower as the carbon mainly contains pores with pore radii larger than about 4000 Å. For PH $V_{ma\text{-}p}$ is 1.13 $cm^3 g^{-1}$, which is much higher than the $V_{ma\text{-}p}$ value of 0.69 $cm^3 g^{-1}$ obtained for S (see data in Table 2). For PH and S the percentage of $V_{ma\text{-}p}$ increase, as calculated as usual in the present study, is 64. As a final comment it should be pointed out that C600 and C900 are essentially macroporous carbonaceous materials.

3.3.3 Density measurements

The values of ρ_{Hg} and ρ_{He} obtained for C600, C900 and ACs are listed in Table 2. ρ_{Hg} must be higher for a less porous carbonaceous adsorbent, whereas the opposite applies to ρ_{He} insofar as the porosity is accessible to helium at room temperature. ρ_{Hg} varies by C900 > C600, CD > A > S, and

PA > ZC > PH. These variation sequences are compatible with a smaller development of porosity in C900 than in C600, which is also reflected by the mercury densities measured for CD and A, and with the presence of a fraction of very narrow porosity in the case of ZC and PH. Concerning ρ_{He}, the variation is C600 > C900, S > CD > A, and PH > PA > ZC, which indicates that the creation of porosity accessible to helium at room temperature was favoured with a decrease in the carbonization temperature and by using steam in the physical activation method and KOH in the chemical activation method. Nevertheless, in connection with the interpretation of the density values it should be taken into account that, especially for PH, PA and ZC, they may be affected by the presence in the samples of heteroatoms coming from the activating agent, owing to its influence on the mass of sample. In Table 2 it is seen that either V_T or $V_{T'}$ is the higher pore volume according to the sample. It was expected that V_T was higher than $V_{T'}$ because of the greater porosity accessible to helium at room temperature than to N_2 at $-196\,°C$. However, as mentioned above, factors other than the measurable porosity may influence the values of ρ_{Hg} and ρ_{He} and hence of V_T. V_T is 1.80 $cm^3 g^{-1}$ for AK and $V_{T'}$ is 1.77 $cm^3 g^{-1}$ for ZC.

3.3.4 Comparison with other ACs

As reported elsewhere (Cookson 1980), in activated carbon the volume of micropores is approximately 0.15–0.50 $cm^3 g^{-1}$ and the volume of macropores is between 0.20 and 0.80 $cm^3 g^{-1}$. The volume of mesopores is relatively small and lies between 0.02 and 0.10 $cm^3 g^{-1}$. For activated carbons with a developed mesoporosity, however, the volume of mesopores may be reach 0.70 $cm^3 g^{-1}$. As seen in Table 2, for ACM the volumes of pores in the three regions of porosity are of the same order of magnitude as for typical activated carbons. By contrast, using VS, ACs are prepared with a better developed porosity, in particular in the regions of meso- and macropores. Thus, V_{mi} is 0.69 $cm^3 g^{-1}$ and V_{me} (or $V_{me\text{-}p}$) is 0.81 $cm^3 g^{-1}$ for ZC and $V_{ma\text{-}p}$ is 1.13 $cm^3 g^{-1}$ for PH.

3.4 Performance of the activating agents

3.4.1 Method of physical activation

In brief, the results obtained in the preparation of ACs from VS by physical activation in air, CO_2 or steam and in the subsequent textural characterization of the resulting products show that the gasification of the carbonized product is a faster process with steam than with air or CO_2 and that with steam not only microporosity develops to a larger degree than with the other activating agents but also meso- and macroporosity significantly increase. In fact, V_T varies by

the order steam > air > CO_2. Similar results were previously reported concerning the relative rate of carbon gasification with steam and CO_2 (Walker et al. 1959; DeGroot and Richards 1989; Moulijn and Kapteijn 1995) and the dependence on burn-off of the textural changes produced by activation of carbonized products in these two atmospheres. Thus, it was earlier stated that the creation of porosity during the activation of carbonized products seems to occur in two steps in which disorganized carbon first (to burn-off 10–20%) and carbon of the aromatic ring system then (at higher burn-off) are burned, the results being the opening of blocked pores in the first case and the production of active sites and wider pores in the second one (Bansal et al. 1988; Wigmans 1989). Furthermore, with steam the predominant mechanism of porosity creation was not only that of pore deepening (increase in pore depth) but also that of pore drilling (increase in pore diameter) (Wigmans 1989). When investigating the use of steam and CO_2 as activating agents in the preparation of activated carbons, it was concluded that steam activation produces a large development of meso- and macroporosity than CO_2 activation, the resulting activated carbon exhibiting a wider pore size distribution (Rodríguez-Reinoso et al. 1995). In the case of pitch-based carbon fibres, it was also found that CO_2 essentially develops microporosity and that steam produces a wider porous texture (Alcañiz-Monge et al. 1994).

The behaviour exhibited by air, CO_2 and steam in the activation process of C600 or C900 may be accounted for if one takes into consideration that these carbonized products are essentially macroporous solids with a substantial mesoporosity development and also that, as usual, their incipient microporosity to a large extent was obstructed or blocked, as suggested by the low micropore volumes (as measured by N_2 adsorption at −196 °C, see data in Table 2). This fact has a special relevance here since microporosity usually plays an outstanding role in gas/solid heterogeneous reactions involving porous materials as most of their surface area concentrates in the micropores. Although microporosity of C600 and C900 was likely more accessible to molecules of the reactant gases under the heating conditions used in the activation process, as compared to the conditions of N_2 adsorption, it may be assumed that the presence of narrow or constricted porosity in C600 and C900 was the main factor in controlling mass transport of the activating agent and therefore its accessibility to reaction sites and as a last resort its activation action (Gómez-Serrano et al. 1996). Probably, diffusion of the activating agent was highly hindered and thereby its molecular shape, size and mass were very important properties in relation to the activation process.

In connection with the above statement it should be mentioned that the CO_2 molecule is linear (O=C=O; C=O bond length, 0.1163 nm), whereas the molecule of water vapour is angular (O−H bond length, 0.0957 nm; angle, 104.5 °)

(Greenwood and Earnshaw 1984). The critical molecular dimension is smaller for steam than for CO_2 (Koresh and Soffer 1980), which results in faster diffusion (Jüntgen 1968) and reaction rate (Walker et al. 1959) with steam than with CO_2. It was also stated that the larger dimension of the CO_2 molecule than of the H_2O molecule results in a restricted accessibility towards the micropores for CO_2 (Thrower et al. 1982). Furthermore, it was suggested that the activation with CO_2 leaves in the carbon structure a larger number of oxygen surface groups than steam and that these groups, in the activated carbons obtained in the early stages of activation (when porosity is still relatively narrow) may act as constrictions of micropores, reducing the effective pore width (Rodríguez-Reinoso et al. 1995). However it should be also borne in mind that linear orientations parallel to the surface become more favourable as the wall separation in slit-shaped pores decreases (Rao et al. 1985) and that this points at that the CO_2 molecule can diffuse in narrower micropores than the steam molecule (Koresh and Soffer 1980).

Although the O_2 molecule is smaller (C=O bond length, 0.121 nm) than the CO_2 molecule, diffusion of the O_2 molecule in narrow porosity of C600 was likely handicapped by the great presence of N_2 in the gas stream of air as the N_2 molecule (N≡N bond length, 0.1094 nm) (Greenwood and Earnshaw 1984) is smaller than the O_2 molecule and as a result the former should move faster than the latter in the aforesaid porosity, and it should render diffusion of the O_2 molecule more difficult. In the case of the steam activation, the effect associated with the presence in the gas stream of N_2, which was the carrier gas, would be mitigated on account of the smaller size of the H_2O molecule. Moreover, the molar mass of the various gases varies by the sequence $CO_2 > O_2 > N_2 > H_2O$ and, according to Graham's law of effusion, their diffusion rate in pores should follow the opposite trend, which agrees with the yield values obtained for the various activating agents in the present study (Table 1).

3.4.2 Method of chemical activation

The performance of H_3PO_4, $ZnCl_2$ and KOH in the preparation of activated carbon has received a great deal of attention on the part of researchers and this has led to the proposal of a variety of mechanisms covering chemical and physical changes produced as a result of the activation process and on the effect of these changes on the creation of porosity. Nevertheless, the proposal of a mechanism for the interaction of the activating agents with a lignocellulosic material such as VS is not an easy task because of the chemical complexity of the systems and of the composition changes undergone by the components of these systems during the whole process of preparation of the ACs (i.e. impregnation and carbonization stages). Thus, concerning the impregnation stage, it should be first taken into account the composition of the impregnation solution. In the case of the H_3PO_4

activation, the phosphorus species present as solutes in such a solution are orthophosphoric acid (H_3PO_4) and polyphosphoric acids, the general formula of which is $H_{n+2}P_nO_{3n+1}$. These phosphorus acids are formed by condensation of H_3PO_4 units, the simplest one being pyrophophoric acid ($H_4P_2O_7$). The presence of polyphosphoric acids in the impregnation solution is favoured with the increase in solution concentration. In the case of $ZnCl_2$, the solution composition is also concentration dependent. Raman studies indicate the presence of $Zn(H_2O)_6^{2+}$, $ZnCl^+$, linear $ZnCl_2$ and $ZnCl_4(H_2O)_2^{2-}$ in aqueous solutions less concentrated than ten molar. The tetrachloro complex dominates for concentrations between ~0.5 to ~10 M, whereas a polymeric species or aggregate was suggested for concentrations higher than 10 M (Irish et al. 1963). Potassium hydroxide is a strong base that in aqueous solution dissociates to K^+ and OH^-. The composition of the impregnation solution is an important factor in connection with its electrolytic action on the lignocellulosic substratum. Thus, for example, $H_4P_2O_7$ is a stronger acid than H_3PO_4, as shown by the values of their first dissociation constant which are 1.4×10^{-1} and 7.5×10^{-3}. Furthermore, the –OH groups in phosphorus acids condense with hydroxyl groups of alcohols to form phosphate esters. Moreover, it should be taken into account that the impregnant concentrates in the lignocellulosic substratum during oven-drying after carrying out the impregnation treatment. When heating the impregnated product in the carbonization stage, H_3PO_4 with the rise of temperature must suffer dehydration and transform into $H_4P_2O_7$ at 215 °C and into HPO_3 at 316 °C (Lazarov 2000). Both phosphorus acids are strong dehydrating agent which may contribute to the dehydration of the lignocellulosic material. In fact, $H_4P_2O_7$ is a useful catalyst for the preparation of olefins by the dehydration of alcohols (Popp and McEwen 1958). On the other hand, $ZnCl_2$ in molten state is found as Zn^{2+} and Cl^- ions (Biggin and Enderby 1981). This substance dissolves readily cellulose only when warmed (Burrage 1933; Ts'ai and Chuang 1942). The KOH melt is ionized to K^+ and OH^- (Charlot and Trémillon 1969; Alexandre-Franco et al. 2010).

In the case of the ACs prepared from VS by the method of chemical activation the yield of the process is higher by the order $ZnCl_2 > H_3PO_4 > KOH$. Micro- and mesoporosity developments are also greater by $ZnCl_2 > H_3PO_4 \gg KOH$. However, macroporosity greatly develops with KOH as compared to $ZnCl_2$ and H_3PO_4. The total porosity varies by the sequence $ZnCl_2 > H_3PO_4 > KOH$. From the N_2 adsorption isotherms (Fig. 1) it follows also that microporosity is heterogeneous in the H_3PO_4 and $ZnCl_2$ activation products. These textural effects are compatible with the dispersion of a larger amount of small size species of zinc and phosphorus in the lignocellusic precursor during the process of preparation of the ACs. In addition, it should be accompanied with a greater concentration of large size species in
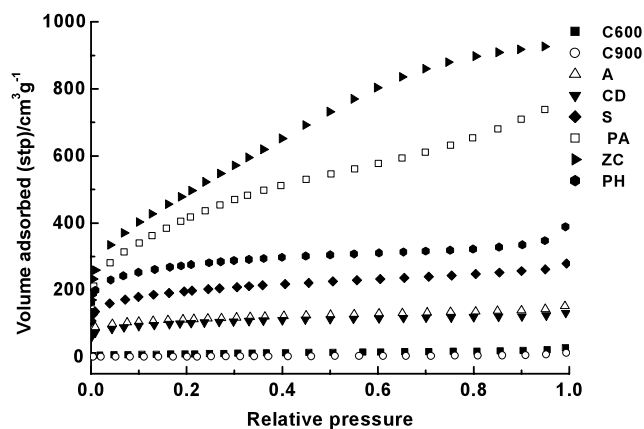

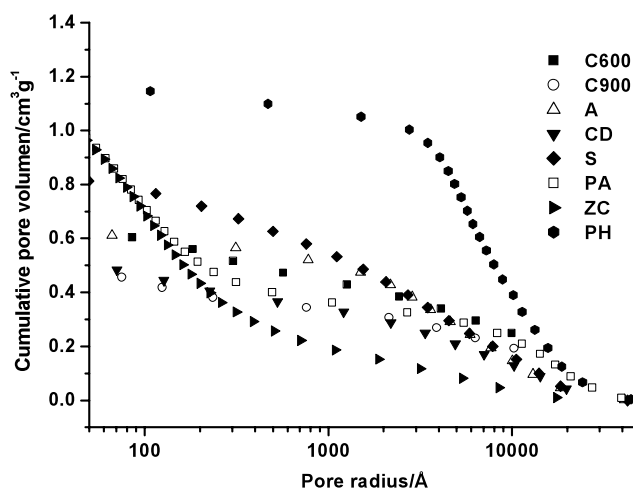
Fig. 1 N_2 adsorption isotherms at −196 °C

Fig. 2 Curves of mercury intrusion (mercury porosimetry)

the material. Probably, the dispersion of species was affected not only by their ionic o molecular size but also by the viscosity of the impregnating fluid and by the heterogeneity of the precursor in its chemical composition, which was made up of hemicellulose, cellulose and lignin as these three components should exhibit a different chemical behavior, like in the case of their thermal behavior as far as carbon yield is concerned (Mackay and Roberts 1982). In this connection it should be taken into account that during the carbonization heat treatment the impregnant melt may diffuse in the transient char due to the creation of porosity on account of the pyrolysis process. In the case of the KOH activation, it seems that a part of the char structure collapsed and this gave rise to creation of large size pores such as macropores. It might be related to a concentration of the K^+ ion locally in some parts of the char structure because of a hindered access to narrow porosity and/or of structural disorder. It is also pertinent to recall here the high reactivity of graphite intercalation compounds, unlike other carbon forms such diamond and graphite. Features of the activation mechanism

concerning the role played by the activating agent in causing chemical and textural changes can be found elsewhere for H_3PO_4 (Molina-Sabio et al. 1995; Jagtoyen and Derbyshire 1998; Suárez-García et al. 2002; Marsh and Rodríguez-Reinoso 2006; Olivares-Marín et al. 2006, and so on), $ZnCl_2$ (Burrage 1933; Rodríguez-Reinoso and Molina-Sabio 1992; Ahmadpour and Do 1997; Marsh and Rodríguez-Reinoso 2006), and KOH (Ahmadpour and Do 1997; Lillo-Ródenas et al. 2003, 2004; Marsh and Rodríguez-Reinoso 2006).

4 Conclusion

From the above results it may be concluded that, under the specific conditions of preparation of AC used in the present study, the yield of the process is much lower for the method of chemical activation than for the method of physical activation. Yield also depends on the activating agent, varying by $CO_2 >$ air > steam and by $ZnCl_2 > H_3PO_4 >$ KOH. The method of chemical activation is more effective than the method of physical activation to prepare AC with a well-developed porous structure. In the first instance, the beneficial effect on the porous structure is stronger with steam than with air and CO_2. In the second instance, greater micro- and mesoporosity developments are obtained with $ZnCl_2$ and H_3PO_4 and of macroporosity with KOH. By the method of chemical activations, ACs with greatly better textural properties than typical activated carbons are prepared. Nevertheless, further research aimed mainly at increasing the yield of the process of preparation of AC from VS by such a method is needed. The performance of the activating agents is analyzed by their pertinent physical and chemical properties. Some insights into the activation mechanisms are also provided.

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