



Activated carbon from cotton stalks by impregnation with phosphoric acid

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Abstract

Dried, crushed cotton stalks were impregnated with varying concentrations of phosphoric acid (20–85 wt.%), dried at 383 K and carbonized at 773 K for 2 h. Porosity was determined by analysis of N₂/77 K adsorption isotherms. High adsorbing carbons with well developed mesoporosity were obtained. Analysis for microporosity, by the α_s -method, proved the presence of minor content in all products. Non-dried impregnated precursor produced a carbon with much lower adsorption capacity, whereas carbonization at 673 K furnished a carbon with comparatively lower texture parameters. TG analysis of the acid-impregnated precursor exhibited considerable modification in the pyrolysis characteristics. The effect of activant was associated with its effect as dehydrant, shift in decomposition to higher temperatures, suppression of volatiles, and space left by its leaching thereafter. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The resolution of ecological problems has recently gained a global significance on account of the increasingly growing pollution of the air and water resources. The need for purification of potable and waste waters from various pollutants, the exhaust gases from sulfur dioxide, the atmosphere from chlorine ions, etc. requires the development of new methods for the production of highly efficient adsorbents.

In this respect carbon adsorbents have attracted special attention on account of their well developed porous structure, large active surface area, and good mechanical properties [1]. Activated carbon adsorbents find many applications on both technical and laboratory scales [2–4]. For example, they are used for the purification of sugar syrups, for oil decolourization and for the improvement of taste and other properties of alcoholic beverages, as well as the purification of waste waters, and in the pharmaceutical and chemical industries [5].

Activated carbon can be prepared from a large number of materials. The most commonly used raw materials in commercial practice are peat, lignite, wood and agricultural by-products. It has been shown

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that activated carbons obtained from agricultural by-products can be favourably compared with other activated carbons used in industry with respect to their adsorptive properties [6]. A wide variety of agricultural precursors have been studied and mentioned in the literature, e.g., apricot stones, nut shells, grape seeds [7–9], maize cobs, rice husk, coconut husk and wood [10], almond and hazelnut shells [6] pine timber and pine scrap [11,12], olive stones and almond shells [13], plum and peach stones [14], and jute sticks [15].

Activated carbons with a wide variety of pore size distribution are obtained by modifying the preparation conditions of either physical or chemical activation process. In both methods there is a reaction of the precursor with the activating agent to develop the porosity, but they differ not only in the practical procedure but also in the mechanism by which the activating agent develops such porosity [16]. In a chemical activation process the lignocellulosic precursor is mixed with a chemical restricting the formation of tar (ZnCl_2 , H_3PO_4 , etc.) and after carbonization and washing the final activated carbon is produced. The chemical incorporated to the interior of the precursor reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinkage of the particle. In this way the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large amount of porosity is formed [17].

A growing interest has been focused, in the last two decades, towards H_3PO_4 as an activating agent in the production of activated carbon from both mineral and botanical sources [18–27]. Previous investigations in our laboratory [9,27–29] proved its effectiveness in producing excellent adsorbing carbons from sugar cane bagasse, apricot stone shells, corn cobs and rice husks. Cotton stalks seem to present an equally attractive carbon precursor as it is found in enormous amounts especially in cotton producing countries. The lack of sufficient information about the utilization of this raw material for carbon production urged the present investigation. It intends to demonstrate its feasibility for obtaining active carbon by impregnation with phosphoric acid, and to characterize its pore structure from nitrogen adsorption.

2. Materials and methods

2.1. Materials

Dried cotton stalks were crushed and ground to be similar in size to sawdust. A total of 60 g of the raw material was thoroughly mixed in a beaker with 150 ml of phosphoric acid with varying concentrations (20–85 wt.%). The slurry was left in a drying oven at 383 K overnight, then transferred to a pyrex glass tube and admitted into an electric tube furnace. Slow heating (ca. 5°C min^{-1}) was achieved to attain 773 K within 2 h, and then soaked at this temperature for 2 h. The cooled product was then washed thoroughly with hot water until the washings show $\text{pH} \geq 6.5$, and finally dried at 383 K (samples 1–6). One additional sample was prepared by impregnation with 40 wt.% H_3PO_4 and introduced directly into the furnace, and heated slowly (ca. 5°C min^{-1}) up to 473 K and kept for 2 h to help release of water and low-temperature volatiles, then temperature raised at a rate of 5°C min^{-1} to 773 K and soaked for 2 h (sample 7). Another sample was impregnated with 50 wt.% H_3PO_4 and heated (5°C min^{-1}) at a lower temperature of 673 K (sample 8). All products were thoroughly washed as usual, dried, and finally kept in screw-cap bottles.

2.2. Techniques and methods of analysis

Thermogravimetry was performed for two samples: the raw powdered cotton stalks and for same soaked in 50 wt.% H_3PO_4 overnight and dried at 383 K. An apparatus of the type Perkin-Elmer 7 Series Thermal Analysis System was employed at a heating rate of 10° min^{-1} up to 1073 K. The result displays both TG and DTG tracings.

The texture of prepared activated carbons was determined by the adsorption of N_2 at 77 K, using an all-glass apparatus of the conventional type. This includes a graduated 100 ml gas burette, a mercury manometer, an adsorption bulb, and a pure N_2 gas reservoir. All apparatus is supplied with high vacuum stopcocks, and connected to a degassing system composed of an oil pump backed with a mercury diffusion pump so as to attain a pressure less than 10^{-4} Torr.

Table 1
Description of prepared carbons and their micropore volumes (ml g⁻¹)

Sample no.	Temperature (K)	wt.% H ₃ PO ₄	V_o^α	V_o^{DR}	V_{super}
CS-1	773	20	0.11	0.25	0.14
CS-2	773	30	0.15	0.37	0.21
CS-3	773	40	0.22	0.49	0.27
CS-4	773	50	0.16	0.45	0.29
CS-5	773	65	0.0	0.43	0.43
CS-6	773	85	0.06	0.36	0.29
CS-7	773	40	0.05	0.30	0.25
CS-8	673	50	0.14	0.32	0.19

The dry, weighed, samples were outgassed for 2 h at 473 K, under a pressure $\leq 10^{-4}$ Torr. Adsorption points at the early pressures were determined after equilibrium with N₂ at 77 K for 15 min or more, and then beyond $P/P^\circ \geq 0.1$ after 5 min.

The equivalent specific surface area was estimated by applying the BET equation (S_{BET}), in the range of $P/P^\circ = 0.05$ –0.30, the total pore volume from the amount of liquid N₂ held at $P/P^\circ = 0.98$, and the mean pore radius from the empirical relation $r = 2V_p/S_{BET}$.

Analysis of the adsorption isotherms was also carried out by the α_s -method [30], whereby three texture parameters were evaluated. (1) Total surface area (S^α) from the slope of the linear relationship of V_{ads} vs. α_s in the region $\alpha_s \leq 1$, extrapolated to zero, (2) the non-microporous surface area (S_n^α) from slope of the intermediate linear section beyond $\alpha_s = 1.0$, and (3) the micropore volume (V_{mic}^α) by extrapolation of the intermediate linear section to the V_{ads} -axis (evaluated as milliliters liquid of N₂). This last parameter (V_{mic}^α) corresponds to the volume of pores of width less than 20 Å.

The mesopore volume was calculated by the method suggested by Gomez-Serrano et al. [31] as equivalent to the volume held in the range of $P/P^\circ = 0.1$ –0.95 (V_{meso}). In fact this will include both super micropores + mesopores as will be shown later. The volume in macropores are obtained from the difference between the total pore volume and volumes contained within micro- and mesopores. The micropore volumes were also estimated from the DR-plot, between $\log V_{ads}$ vs. $\log^2 P^\circ/P$ [32]. According to these authors, the intercept of the linear plot at the low pressure should give the volume of

micropores (V_{mic}^{DR}). In the present case this was tried within $P/P^\circ = 0.01$ and 0.20.

3. Results and discussion

Six of the prepared carbons are heated at 778 K, but pre-impregnated with varying concentrations of H₃PO₄ ranging between 20 and 85% (samples 1–6) (cf. Table 1). Carbon 7 was introduced directly to furnace and dried in situ for 2 h at 473 K then temperature raised also to 773 K. Carbon 8 is impregnated with 50% H₃PO₄ and heated at 673 K. Fig. 2 displays the N₂-77 adsorption isotherms. These show isotherms (Fig. 1) belonging to type I + II of the BDDT-classification. As the mesoporosity of the carbon is developed by enlargement of the microporosity, the slope of plateau in the N₂ adsorption isotherm will increase giving the apparent type I + II isotherm. Carbons 5 and 6, particularly show high increasing slope at high pressures suggesting higher mesoporosity and macroporosity.

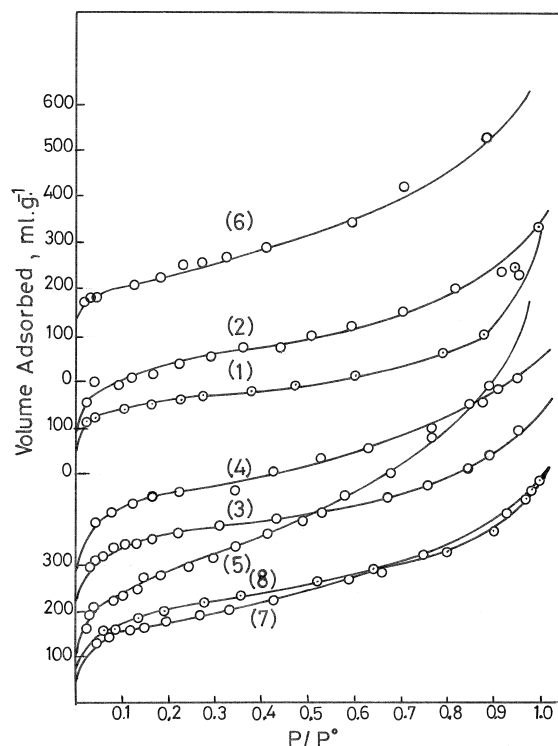


Fig. 1. Adsorption isotherms of N₂ at 77 K of activated carbons.

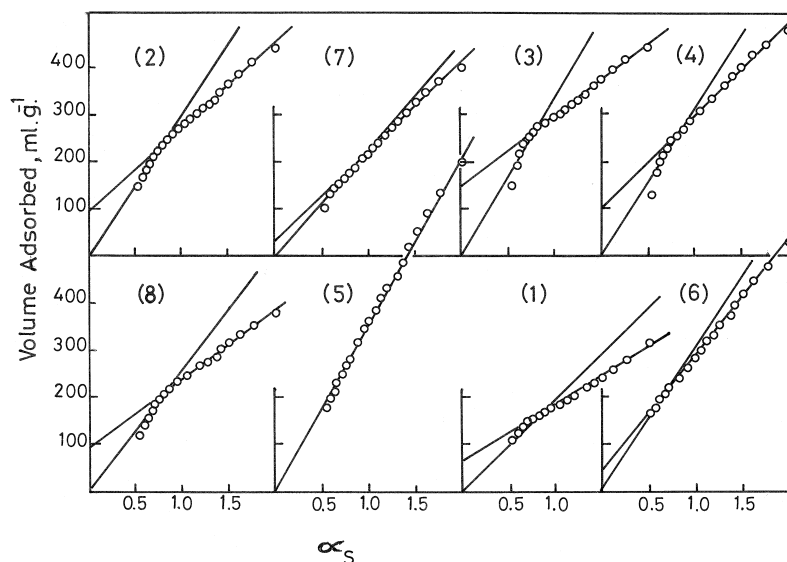


Fig. 2. α_s -Plots for N_2 adsorption at 77 K of activated carbons.

Fig. 2 presents the α_s -plots of the eight carbons. According to the classification given by Selles-Perez and Martin-Martinez [33] seven of the α_s -plots belong to the group $\alpha - 1b$. This indicates development in the mesoporosity of different degrees as evident from the varying slopes of the intermediate straight lines. Carbon 5 exhibits an extraordinary behaviour shown by the appearance of a single straight line extending all over the whole pressure range, indicating the absence of microporosity. This means that the α_s -plots reflect the changes in carbon porosity as function of introduced activant. Increased phosphoric acid inflects increasing action on the raw

material, such that at 65 wt.%, and beyond the intense effect helps in considerable gasification with generation of porosity in the supermicro-, meso-, and macropore ranges as will be illustrated in next sections. In the case of carbons 5, 6 and 7, unhindered layer formation will take place.

3.1. Comparison between the different estimates of micropore volume

Table 1 gives the micropore volumes estimated by the two suggested procedures, the lowest values belong to the α_s -method, whereas DR estimates are

Table 2
Some texture parameters of the prepared activated carbons

Sample no.	S_{BET} ($m^2 g^{-1}$)	V_p ($ml g^{-1}$)	r (\AA)	S^α ($m^2 g^{-1}$)	S_n^α ($m^2 g^{-1}$)	V_{meso} ($ml g^{-1}$)	V_{macro} ($ml g^{-1}$)
CS-1	524	0.79	28.8	549	318	0.38	0.30
CS-2	860	0.83	19.9	835	492	0.44	0.24
CS-3	938	0.82	17.6	938	422	0.38	0.21
CS-4	858	0.86	19.9	863	542	0.43	0.27
CS-5	1032	1.43	29.1	985	980	0.85	0.58
CS-6	810	1.01	23.9	847	682	0.57	0.37
CS-7	639	0.75	23.7	633	577	0.43	0.26
CS-8	747	0.76	21.1	717	408	0.37	0.24

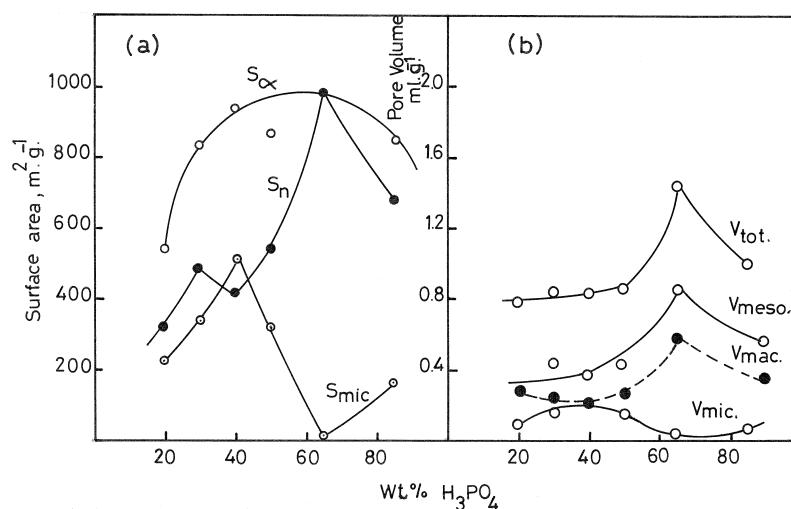


Fig. 3. Variation in (a) surface area (S_α and $S_{\alpha n}$) and (b) pore volumes (total, meso, macro and micro), as function of impregnating acid concentration.

much higher. However, the last estimation seems to be unreasonable as the values fall much beyond the monolayer capacity that appear at $P/P^\circ = 0.04$ – 0.09 . The DR values fall at much higher relative pressures (0.19 – $0.45 P^\circ$), which seem to invalidate this method for evaluating the micropore volume. It has been suggested [30] that the α_s -method, measures the narrow microporosity (ultrapores) whereas the DR-method estimates both of the micropores and

narrow mesopores (ultrapores and supermicropores). Accordingly, the microporosity of the present carbons was limited to the α_s -method as its values appear at reasonably low pressures (below $0.02 P^\circ$). This means that the narrow micropores fill at such very low pressure before pore filling in wider micropores and mesopores start to occur. This has been the basic assumption of the early micropore filling theory developed by Dubinin [32].

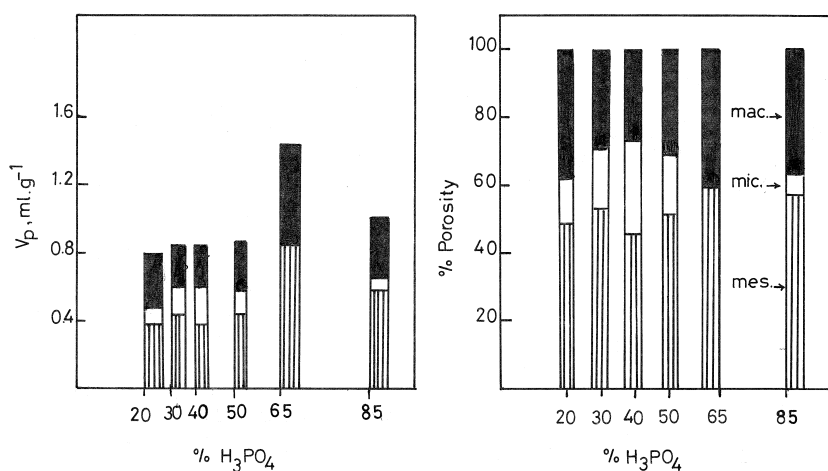


Fig. 4. Distribution of pore volumes within different pore sizes (total, macro, meso and micropores).

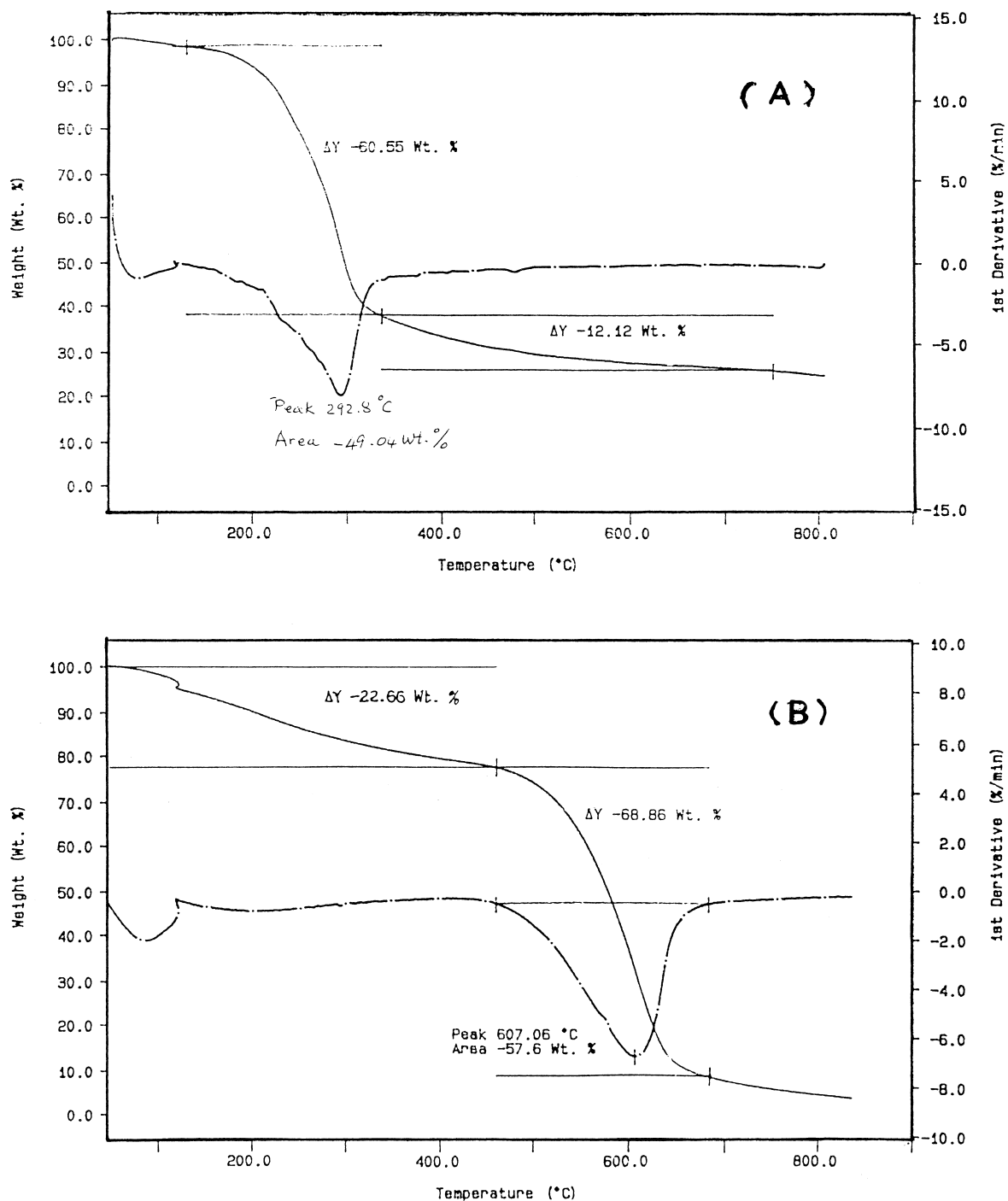


Fig. 5. TG-DTG diagram for (A) raw cotton stalks and (B) 50% H_3PO_4 -treated cotton stalks.

3.2. Variation in texture parameters with increased acid concentration

Table 2 summarizes some of the texture parameters, which are graphically presented in Fig. 3a,b. Increased acid concentration is associated with an increased development in total surface area, mesoporous area, total pore volume, mesoporous volume and macroporous volume. This is true up to 65 wt.% H_3PO_4 , but a higher concentration of 85 wt.% is associated with a decrease in all texture parameters. An approximate decrease in micropore volume appears with respective increase in activant concentration. It is noticeable that all the carbons 2 to 6 are high surface area products characterised by more or less same value ($895 \text{ m}^2 \text{ g}^{-1}$, $\sigma_n = 58 \text{ m}^2 \text{ g}^{-1}$). Only carbon 1 obtained at the lowest acid concentration (20 wt.%) exhibits a relatively low value of $550 \text{ m}^2 \text{ g}^{-1}$.

This means that increased acid concentration up to 65 wt.% H_3PO_4 is associated with development in porosity characteristics, except the microporosity. At 85 wt.% H_3PO_4 , the dehydrated excess acid seems to form a protecting layer that partly prevents the effect of the surrounding atmosphere and thus inhibits free formation of the internal porosity. Moreover, a possible residual phosphate blocks some of the created porosity thus becomes inaccessible to the nitrogen molecules. It has been observed, with other carbon precursors [9,27–29], that the ash content increased considerably at high acid concentrations which will, in this case, occupy internal porosity. External burning could be the predominant mechanism of activation in such case.

An illustrative presentation of the present data appears in Fig. 4, showing the percent distribution of pores within the different pore size species. Activated carbons obtained from cotton stalks by H_3PO_4 -activation, and heat treated at 773 K, are essentially meso-macroporous. Micropores constitute a low percent of the total pore system (0–20%). It is remarkable that the 65 wt.% H_3PO_4 -activated carbon seems, to exhibit no volume within the micropores.

3.3. Effect of changing conditions of preparation on texture

One samples was impregnated with 50 wt.% of H_3PO_4 and carbonized at 673 K (CS-8) so as to be

compared with same (CS-4) carbonized at 773 K (cf. Table 2). Heating at a lower temperature produces an equally active carbon but with lower values of the principal texture parameters. Carbonization at a higher temperature helps to the free removal of volatile matter and to development of the porosity.

Another carbon (CS-7) prepared by impregnation and direct carbonization in same day, is characterized by much lower porosity. The predried impregnated material (CS-4) produces under similar conditions an activated carbon of superior adsorption characteristics and much developed microporosity as well. Predrying plays a critical role in determining the characteristics of the produced carbon. It leads to better impregnation of the precursor through efficient diffusion of the acid and its interaction with the lignocellulosic components.

3.4. Influence of H_3PO_4 on the thermal pyrolysis of cotton stalks

Fig. 5 represents the TG-DTG tracings for both raw cotton stalks and its acid-treated material (a, b). Impregnation with phosphoric brings about remarkable modifications to the course of pyrolysis and characteristics. Thus, (i) it shifts the main decomposition peak of the raw material indicating delayed pyrolysis from 566 to 880 K; (ii) it increases the total weight loss up to 973 K (cf. 91.6 and 72.6%) as a result of promoted gasification of the carbonaceous material; (iii) it leads to the formation of lower char (part of it belongs to ash and residual dehydrated H_3PO_4).

Comparison of the two traces at 500°C (773 K) indicates that the untreated stalks lose $\sim 70\%$, whereas the acid-impregnated stalks lose only $\sim 25\%$. Thus, here the acid delays mass decomposition with consequent formation of higher carbon-product at this specific temperature.

4. Conclusions

Activation with phosphoric acid offers many recommending advantages: it is a one-step process, effective at low temperature, results in a higher carbon yield, and partial recovery of activant is possible. Its action as activant could be attributed to

several effects: (i) its effect as a dehydrating agent; (ii) it inhibits formation of tar and thus enhances formation of char; (iii) it produces chemical and physical changes that modify the degradation process (it weakens the structure, increases elasticity and swelling of the particles); and (iv) upon intense washing of the product an elimination of the deeply situated activant leads to the appearance of the tremendous porosity [24,34]. It was suggested by Laine and Calafat [35] that phosphoric acid forms, in addition, a 'skin' of phosphate protecting the internal carbon structure and thus protecting the product from excessive burn-off leading to surface area decrease.

The notation 55 (50% H_3PO_4 , 500°C) condition noticed as effective with other carbon precursors (sugar cane bagasse [27], apricot stone shells [9], corn cobs [29], and rice hulls [28]) proved also effective with the present carbon obtained from cotton stalks. The amount of phosphoric acid incorporated into the precursors (50 wt.% H_3PO_4) seems to be enough and efficient to attain good impregnation. On the other hand, a temperature of 773 K lies above the pyrolysis temperature of many carbon precursors and seems also effective in carbonization of the lignocellulosic matrix with sufficient devolatilization of the volatile products. In fact, the presence of incorporated phosphoric acid brings about a shift in the decomposition temperature ($\sim 300^\circ\text{C}$) which prevents the burn-off of char and raises its yield.

It is thus demonstrated that a temperature of 773 K is suitable for the production of activated carbon from cotton stalks by pre-impregnation with phosphoric acid (30–65 wt.%). Carbons with well developed mesoporosity and high surface area are obtained that seem promising for the adsorption from solution. A lower temperature of 673 K produces a carbon with relatively lower surface area and porosity. Predrying of the impregnated mass before carbonization is most suitable to obtain better active carbon characterised by much developed porosity.

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