



Preparation of activated carbons from Spanish anthracite

I. Activation by KOH

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Abstract

In a previous work, the use of a Spanish anthracite for the preparation of activated carbons by chemical activation was analyzed. The results indicated that this raw material is promising for that purpose. In the present paper, that previous work is extended and the effect of different preparation variables on the final porous texture is discussed, such as KOH/anthracite ratio, heating rate, carbonization temperature and carbonization time. Among those different variables studied, the KOH/anthracite ratio seems to be the most important one. In addition, this study introduces an investigation of the nitrogen flow rate, showing that this variable has a very important effect on porosity development. The study confirms that the raw material used is appropriate for the preparation of activated carbons in a single stage pyrolysis process. The proper choice of the preparation conditions allows us to produce microporous activated carbons with a micropore volume up to $1.45 \text{ cm}^3/\text{g}$ and a BET surface area of $3290 \text{ m}^2/\text{g}$. This work is extended in Part II with a detailed study using NaOH as activating agent and a different preparation method (physical mixing). © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Adsorbents are required in many different applications, in either liquid or gas phase processes. Activated carbons are widely used as adsorbents in technologies related to pollution abatement due to their highly porous texture and large adsorption capacity [1–3].

However, controlled pore size and pore size distribution are necessary for the application of those materials in a specific end use. The porous texture of the activated carbons depends strongly on both, the activation process and the nature of the precursor.

Basically, there are two different processes for the preparation of activated carbons [1,2], the so-called physical and chemical activation. Physical activation involves carbonization of a carbonaceous precursor followed by gasification of the resulting char or direct activation of the starting material in the presence of an activating agent such as CO_2 , steam or a combination of both. This gasification or activation process eliminates selectively the most reac-

tive carbon atoms of the structure generating the porosity. On the other hand, in chemical activation the precursor is impregnated with a given chemical agent and, after that, is pyrolyzed. As a result of the pyrolysis process, a much richer carbon content material with a much more ordered structure is produced, and once the chemical agent is eliminated after the heat treatment, the porosity is so much developed. Several activating agents have been reported for the chemical activation process: phosphoric acid, zinc chloride and alkaline metal compounds [1–13]. Phosphoric acid and zinc chloride are activating agents usually used for the activation of lignocellulosic materials which have not been previously carbonized [9,10]. Contrarily, alkaline metal compounds, usually KOH, are used for the activation of coal precursors or chars [6,11]. In the literature we can see that there is a growing interest in alkaline hydroxide activation process and KOH has been found to be one of the most effective compounds in the production of activated carbons [12,13].

An important advantage of chemical activation is that the process normally takes place at a lower temperature and shorter time than those used in physical activation. In addition, it allows us to obtain very high surface area activated carbons. Moreover, the yields of carbon in

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chemical activation are usually higher than in physical activation because the chemical agents used are substances with dehydrogenation properties that inhibit formation of tar and reduce the production of other volatile products [9,11]. However, the general mechanism for the chemical activation is not so well understood as for the physical activation. Other disadvantages of chemical activation process are the need of an important washing step because of the incorporation of impurities coming from the activating agent, which may affect the chemical properties of the activated carbon [14], and the corrosiveness of the chemical activation process [15].

The literature also shows several differences in the porous texture of activated carbons prepared using physical or chemical activation methods, i.e., the extent of the porosity development and the pore size distribution [11].

Regarding the precursor of activated carbons, as we have commented before, there are two main sources for the production of commercial activated carbons: coal and lignocellulosic materials. The use of Spanish coals as feedstock for the production of activated carbons is of interest to our country due to the large coal production (31.3 metric tons in 1993) and reserves [6]. Among a wide range of coal precursors, anthracites are of interest because of their abundance, low cost and high carbon content.

As we have said, the properties of activated carbons depend on the activation process and the nature of the raw materials. Moreover, in both activation processes, physical and chemical, a knowledge of different variables during the activation is very important in developing the porosity of the carbon. Because of the more complex mechanism in the case of chemical activation, the effect of each experimental variable should be more extensively studied.

In a previous study [6], the chemical activation of Spanish coals with hydroxides was analysed. It was shown that anthracite produces activated carbons with an exceptionally narrow pore size distribution and that KOH is a very effective activating agent for coal activation.

The objective of the present paper is to continue that previous work using an anthracite as a precursor and KOH as activating agent. We concentrated on the evaluation of these different variables: the effect of agent/coal ratio, heating rate, temperature and time of pyrolysis. In addition, we studied new variables in the preparation process such as the effect of nitrogen flow rate and the effect of washing stage conditions (acid versus water washing).

2. Experimental

A Spanish anthracite with an 11 wt% of ash content was used as the precursor in the present study. The precursor was ground and sieved to a particle size range of 600–1000 μm .

Chemical activation with KOH was carried out using an impregnation method. Two grams of anthracite were

mixed, by stirring with a solution that contained 10 ml of water and 1, 2, 3, 4 or 5 g of the activating agent depending on the ratio of activating agent/coal (A/C) used (1:1, 2:1, 3:1, 4:1 or 5:1) for 2 h at 60°C. The resulting slurry was dried at 110°C overnight in an oven. Then, the resulting mixture was used for carbonization.

The carbonization was carried out in a horizontal furnace and the samples were heated (5 or 20°C/min) from room temperature to the final carbonization temperature (T_{carb}) in different nitrogen flows (80, 200, 400 or 800 ml/min). Samples were kept at the final temperature for different carbonization times (t_{carb}) of 0.5, 1 or 2 h before cooling down under nitrogen.

The pyrolyzed samples were washed repeatedly with a 5 M solution of HCl and later with distilled water until free of chloride ions. In order to evaluate the effect of the washing process, some of the samples were washed directly with distilled water. Once the activating agent was removed, the sample was dried at 110°C for 12 h.

The porous texture characterization of all the samples was carried out by physical adsorption of gases (N_2 at 77 K and CO_2 at 273 K) using an automatic adsorption system (Autosorb-6, Quantachrome). Micropore volumes have been calculated from the adsorption isotherms of nitrogen and carbon dioxide applying the Dubinin-Radushkevich (DR) equation.

3. Results and discussion

In a chemical activation process many parameters exist, even keeping the precursor and the activating agent constant is important, that affect the porous texture of the activated carbon. In the present study we present the effect of different parameters involved in a chemical activation process on the porosity of the final activated carbon. The nomenclature of the samples includes the identification of the anthracite (UA) and the activating agent (K), followed by a number indicating the KOH/anthracite ratio. Finally, the nitrogen flow rate is included. As an example, sample UAK2-800 was prepared using the impregnation method with a 2:1 KOH/anthracite ratio, a nitrogen flow rate of 800 ml/min and a heating rate of 5°C/min, up to 700°C, over 1 h. We have always changed one of those parameters, keeping the rest constant. In the nomenclature of the samples, the carbonization conditions (heating rate, pyrolysis temperature, pyrolysis time) have not been included. For that reason, a letter has been added at the end of the name of the sample, indicating that only a variable (heating rate, pyrolysis temperature or pyrolysis time) has been modified (for example UAK2-800a, UAK2-800b, UAK2-800c and UAK2-800d).

3.1. Effect of KOH/anthracite ratio

The agent/coal ratio has been found to be the most

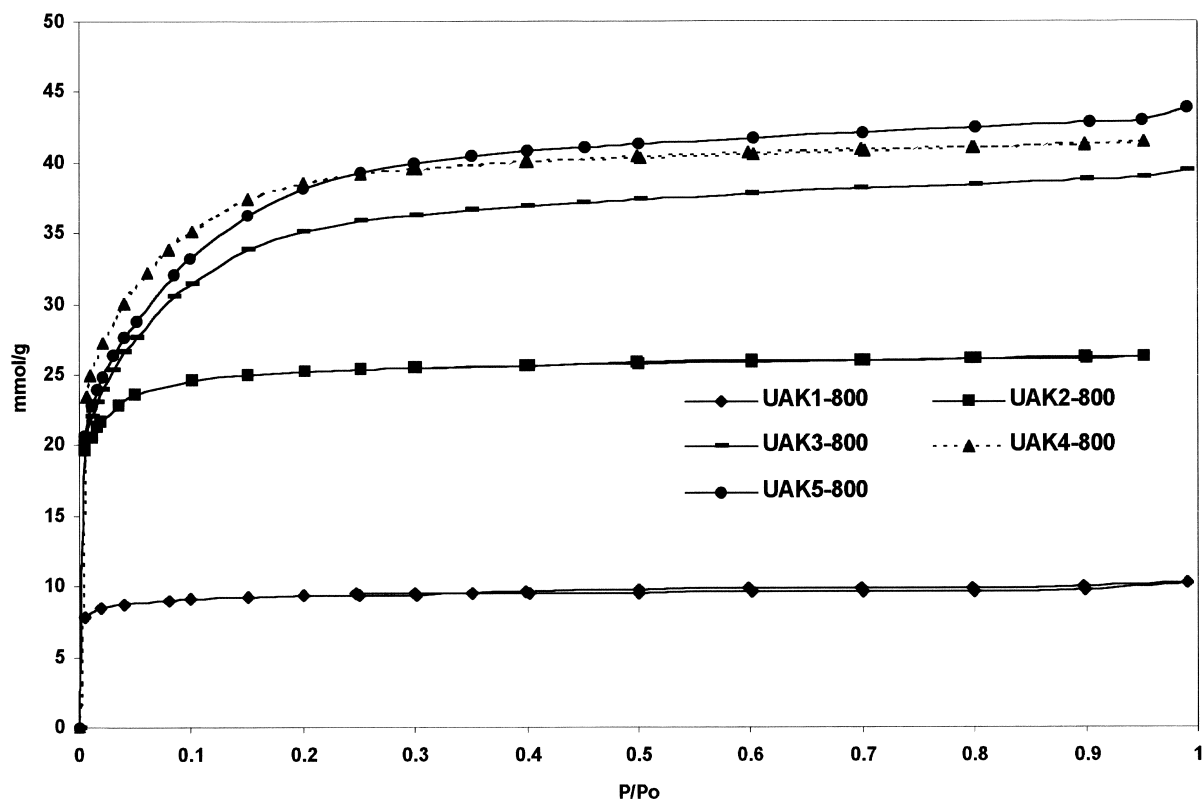


Fig. 1. N_2 adsorption isotherms at 77 K. Effect of KOH/anthracite ratio.

important parameter in a chemical activation process [8,9]. Fig. 1 shows the effect of KOH/anthracite ratio on the nitrogen adsorption isotherms. It shows that an increase in the KOH/anthracite ratio produces a great enhancement of N_2 adsorption capacity at 77 K. Table 1 contains the porous texture characterization results obtained by applying the BET equation to N_2 adsorption at 77 K and the DR equation to N_2 adsorption at 77 K and CO_2 adsorption at 273 K. It can be seen that surface area and micropore volume both increase continuously with increasing chemical ratio, reaching a maximum for the KOH/anthracite ratio of 4:1. This fact is shown in Fig. 2, where the BET surface area is plotted versus KOH/anthracite ratio. Thus, at high KOH/coal ratios the effect of the metallic salt in

the formation of microporosity is more pronounced reaching a maximum value for a KOH/anthracite ratio of 4:1. In a recent study [16], the results corresponding to the activation with KOH of a bituminous coal have been presented. It has been seen that for the activated carbon carbonized at 700°C the highest porosity is obtained with a chemical ratio of six. However, with an activation temperature of 800°C the optimum chemical ratio for preparing high porosity carbons has been found to be 4.25. In our case, a lower chemical ratio (chemical ratio of four) is the optimum in the case of using a carbonization temperature of 700°C. This fact indicates that maybe because of the different raw material or/and because of the much higher nitrogen flow rate used (the important effect of the

Table 1

Effect of KOH/anthracite ratio on porous texture (5°C/min, 800 ml/min, 700°C, 1 h)

Sample	KOH/anthr ratio	$V(CO_2)$ (cm^3/g)	$V(N_2)$ (cm^3/g)	$V(N_2) - V(CO_2)$	BET surface area (m^2/g)	Micropore contribution
UAK1-800	1:1	0.37	0.33	<0	726	0.92
UAK2-800	2:1	0.86	0.89	0.03	2021	0.93
UAK3-800	3:1	0.72	1.35	0.63	2758	0.81
UAK4-800	4:1	0.81	1.45	0.64	3290	0.85
UAK5-800	5:1	0.73	1.44	0.71	3183	0.77

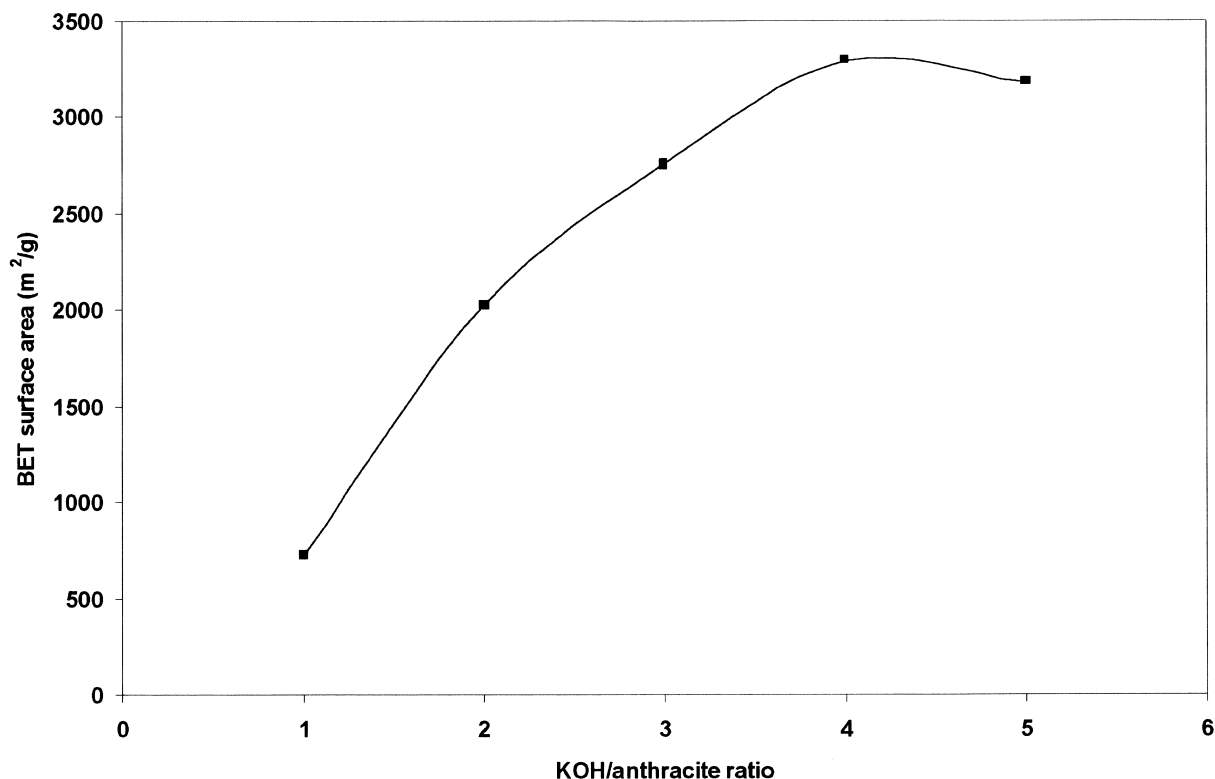


Fig. 2. Evolution of the BET surface area with the KOH/anthracite ratio.

nitrogen flow rate will be present later), in our case, less aggressive conditions, e.g., lower carbonization temperature and lower chemical ratio, are necessary to obtain an activated carbon with a high porosity.

In chemical activation it is important to study the effect of agent/coal ratio not only on micropore volume and surface area, but also on the micropore size distribution. In the literature [8,10] it was shown that in chemical activation there are two different mechanisms: the first one is the micropore formation which starts with the addition of chemicals to the raw materials and the second one is the pore widening which is the result of the chemical effect inside the opened pores. Pore widening normally begins when there are a number of opened pores in the structure, therefore, it starts to be significant when the chemical ratio is reasonably high. In order to determine the relative contribution of each mechanism in the case of KOH, the micropore volume calculated from N_2 and CO_2 data have been compared. The micropore volume calculated from CO_2 adsorption at 273 K (V_{CO_2}) gives us the volume of narrow microporosity (pore size smaller than approximately 0.7 nm) [17–20] while the micropore volume assessed from N_2 adsorption provides the total micropore volume (V_{N_2}) (pore size lower than 2 nm). The densities used for liquid N_2 at 77 K and adsorbed CO_2 at 273 K were, respectively, 0.808 and 1.023 g/ml [17–20]. Table 1

shows that the sample with the lowest difference between the micropore volume calculated from N_2 and CO_2 data is the sample with carbon/KOH ratio of 1:1. Thus this material has the narrowest micropore size distribution. Table 1 also shows that the higher the KOH/anthracite ratio, the higher the differences between the micropore volume calculated by those two different ways, suggesting that the micropore size distribution is getting wider. This change in the micropore size distribution can be also seen in the knees of the N_2 isotherms (Fig. 1); the higher the KOH/carbon ratio, the wider the knee of the isotherm. It is even shown an overlap between the curves corresponding to the samples with the highest KOH/anthracite ratios due to the much wider pore size distribution presented by the sample with a 5:1 ratio. Thus, the KOH/anthracite ratio not only affects the micropore volume but also to the micropore size distribution. This is a factor, which should be taken into account for the end use of the activated carbon.

In addition, from N_2 adsorption data the micropore contribution can be calculated. That estimation has been obtained by dividing the amount of nitrogen adsorbed at a relative pressure of 0.1 to the amount adsorbed at a relative pressure of 0.95 from the nitrogen isotherm data at 77 K (Table 1) [8]. It can be seen that the micropore contribution is very similar for the 1:1 and 2:1 ratios, and this

micropore contribution decreases with the KOH/anthracite ratio. In the case of the sample UAK5-800, the micropore contribution is still quite high. Thus, it can be said that for KOH, the micropore creation plays an important role in the whole range of the KOH/anthracite ratios studied. This agrees with the conclusion of Ahmadpour and Do [8]. It can also be observed that the sample with the higher difference between micropore volume calculated by N₂ and CO₂ data (UAK5-800) is also the sample with the lowest micropore contribution, indicating the wider pore size distribution (see Table 1).

3.2. Effect of heat treatment

Four different parameters are involved in heat treatment: heating rate, temperature and time of pyrolysis and nitrogen flow rate during pyrolysis. Three of these are discussed in this section. The effect of nitrogen flow rate is analysed in the next section because this important variable has hardly ever been described.

Table 2 contains the porous texture results of the activated carbons obtained by changing those parameters. If we compare the effect of the heating rate during the pyrolysis, it can be seen that the lower the heating rate the higher the micropore volume of the activated carbons. During the heating process, KOH melts (melting point of KOH is 360°C), then, it is reasonable that a lower heating rate allows a better contact between the carbon and the melted KOH before the reaction temperature is reached. In addition, it is known [6,8] that in KOH activation, some surface oxygen complexes are produced which are responsible for further carbon gasification and release of gaseous products such as CO₂, CO, etc. Then, a lower heating rate will produce a slower and more controlled evolution of gaseous products, which could also explain the better microporosity development when a lower heating rate is used.

Table 2 also presents the effect of activation temperature and time. In the previous work [6] the results for two temperatures (500 and 700°C) were presented. In the present study higher temperatures are tested (700 and 800°C). It can be observed that a chemically activated carbon with higher micropore volume is obtained using a higher temperature (800°C) and a longer time. This is

expected from previous results [21]. However, as in the case of the effect of the KOH/carbon ratio, the higher temperature and time of pyrolysis produce a wider micropore size distribution, which would not be suitable for some applications (see micropore volume from CO₂ and N₂ data in Table 2).

3.3. Effect of nitrogen flow rate

In most of the previous chemical activation studies the effect of nitrogen flow rate has not been studied or the modification of the nitrogen flow rate has been very small. In the present study, the results corresponding to a high variation of nitrogen flow rate are presented. Fig. 3 shows the N₂ adsorption isotherms for samples prepared using nitrogen flow rates from 80 to 800 ml/min. All these samples have been prepared using a KOH/anthracite ratio of 2:1 and a carbonization process at 700°C for 1 h. It can be observed that even though all the preparation parameters are the same the different nitrogen flow rates change the porous texture of the samples drastically. Activated carbons with much higher adsorption capacities and much higher micropore volumes (see Fig. 3 and Table 3) are obtained using higher nitrogen flow rates. It should be emphasized that for a 2:1 KOH/anthracite ratio, an increase of the nitrogen flow rate from 80 to 800 ml/min produces an activated carbon with more than double the micropore volume and surface area.

Given the substantial effect of the nitrogen flow rate on the final porosity of the activated carbon, the same study was done for activated carbons prepared with a higher KOH/anthracite ratio (4:1). Fig. 4 shows the N₂ adsorption isotherms of the samples prepared with different nitrogen flow rates and Table 3 contains the results of porous texture analysis for these samples. It can be seen that for a much higher KOH/anthracite ratio (4:1) the effect of the nitrogen flow rate in the porous texture of the activated carbon is still important, although somewhat less significantly than for the lower ratio (2:1). Anyway, it is shown that the same trend is obtained as for the samples with the ratio 2:1.

These results indicate that a faster removal of the gases evolved during the carbonization process favours the

Table 2
Effect of heat treatment conditions on porous texture (KOH/anthracite=2:1, 800 ml/min)

Sample	Heating rate (°C/min)	Carbonization temperature (°C)	Carbonization time (h)	V (CO ₂) (cm ³ /g)	V (N ₂) (cm ³ /g)	BET (m ² /g)
UAK2-800	5	700	1.0	0.86	0.89	2021
UAK2-800a	20	700	1.0	0.77	0.85	1851
UAK2-800b	5	800	1.0	0.81	0.96	2085
UAK2-800c	5	700	0.5	0.80	0.80	1784
UAK2-800d	5	700	2.0	0.86	0.91	2111

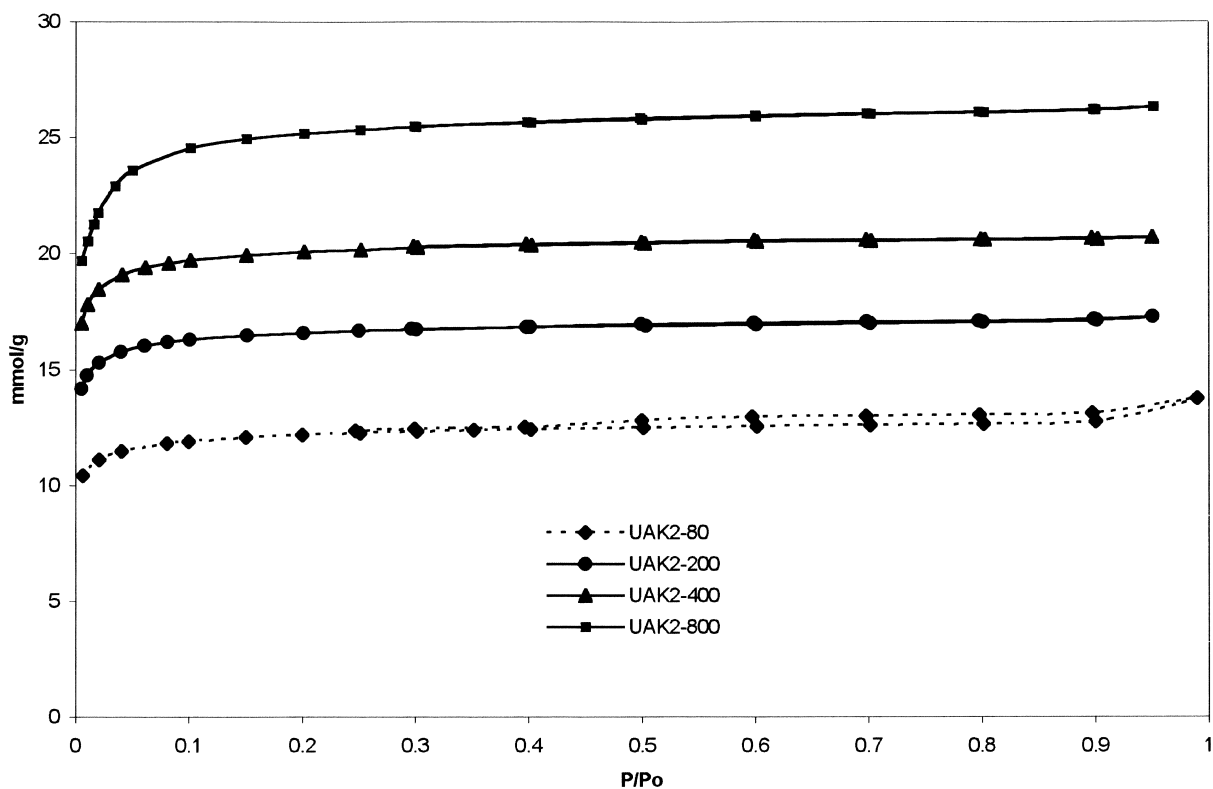


Fig. 3. N_2 adsorption isotherms at 77 K. Effect of nitrogen flow rate during the pyrolysis process for the activated carbons with KOH/carbon ratio of 2:1.

creation of micropores or, in other words, a lower concentration of these gases produces higher micropore development. This could be related to the results presented in the previous section where it was shown that the lower the heating rate, the higher the micropore volume. In the case of using a lower heating rate, the evolution of gases during the carbonization process is slower, resulting in a lower concentration of gases.

Table 3

Effect of nitrogen flow rate on porous texture (KOH/anthracite = 2:1, 5°C/min, 700°C, 1 h)

Sample	N_2 Flow rate (ml/min)	$V(CO_2)$ (cm ³ /g)	$V(N_2)$ (cm ³ /g)	BET surface area (m ² /g)
UAK2-80	80	0.43	0.43	945
UAK2-200	200	0.61	0.58	1305
UAK2-400	400	0.73	0.71	1580
UAK2-800	800	0.86	0.89	2021
UAK4-200	200	0.69	1.28	2637
UAK4-400	400	0.70	1.34	2817
UAK4-800	800	0.81	1.45	3290

Another possible explanation to this phenomenon that needs to be studied could be related to the production of potassium during the pyrolysis process. At 700°C deposition of potassium on the cooler parts of the furnace has been observed. This potassium is evolved during the reaction between carbon and KOH. If this potassium is removed from the reaction place (using a high nitrogen flow rate), the equilibrium of the reaction is displaced to the production of further potassium and then, an increase in the degree of reaction between carbon and KOH could occur.

With these results, it can be said that the nitrogen flow rate is a very important parameter that has to be taken into account during the preparation of activated carbons by KOH activation. This experimental variable has an important effect on the final porous texture of the activated carbon for all the KOH/anthracite ratios. Intriguingly, the literature does not present evidence of the importance of such a variable. Presumably, the effect of this parameter on the final porosity of the carbon depends on the type of furnace used for the preparation of the sample and also on the geometrical distribution of the carbon with respect to the N_2 stream. Further work is being carried out to analyze those possibilities.

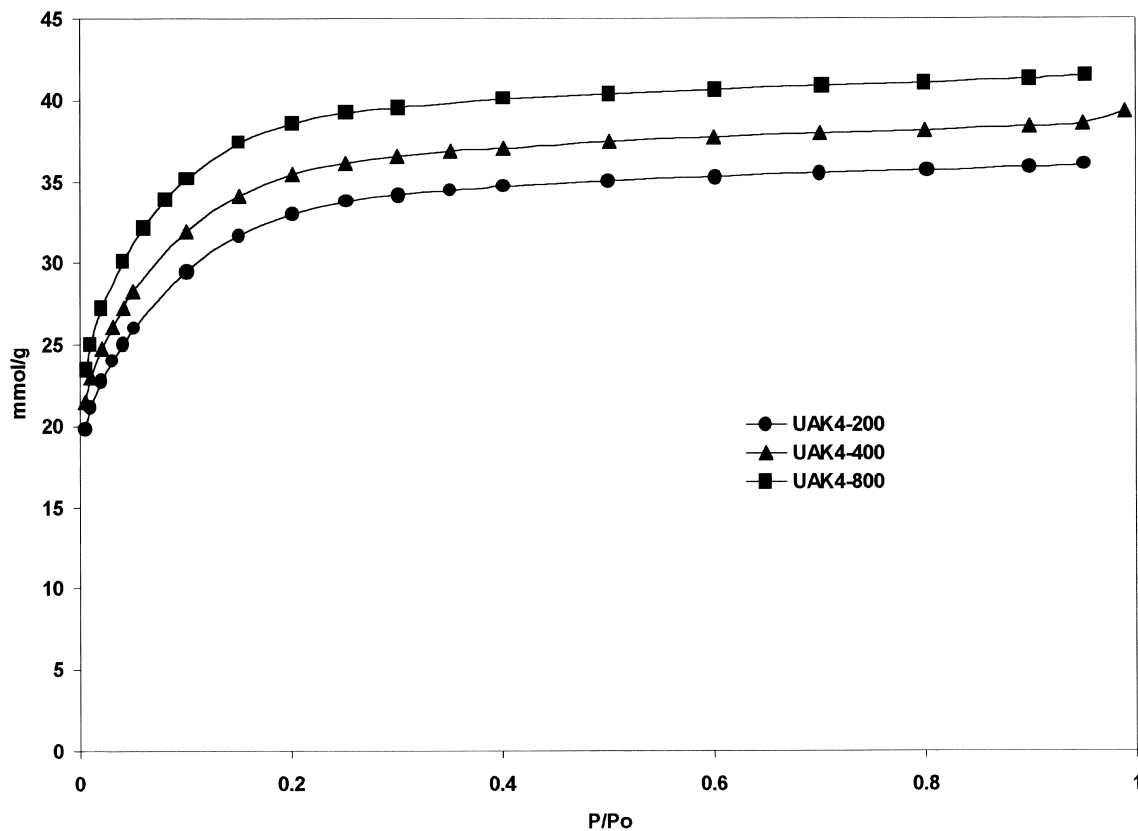


Fig. 4. N_2 adsorption isotherms at 77 K. Effect of nitrogen flow rate during the pyrolysis process for the activated carbons with KOH/carbon ratio of 4:1.

3.4. Effect of washing stage

The washing stage is the last step in the preparation of a chemically activated carbon. The pyrolyzed mixture is leached in water or acid solutions to remove the activating agent. In order to see the effect of the washing step, one sample has been characterized after being (i) carbonized, (ii) washed several times with distilled water and (iii) washed several times with 5 M hydrochloric acid and, after that, washed several times with distilled water. Fig. 5 presents the N_2 adsorption isotherms corresponding to the three cases. The plot clearly shows that the unwashed sample does not show any N_2 adsorption. This indicates that the porosity created in the carbon samples is blocked by the potassium compounds that must be removed to obtain an accessible microporosity. In Fig. 5, it can be also observed that after washing with water, a substantial increase in the N_2 adsorption capacity results. It means that most of the KOH is removed with water. However, the sample washed using hydrochloric acid presents a somewhat higher N_2 adsorption indicative of a better removal of the potassium compounds by the HCl washing. In addition,

an ash estimation of those two washed activated carbons has been done. An ash content of 7 wt% for the sample washed only with water and <1 wt% for the sample washed with water and hydrochloric acid has been found. It is important to note that, from an industrial point of view and depending on the final use of the activated carbon, an acid washing could be avoided as it can be clearly seen in Fig. 6. Fig. 6 illustrates the micropore volume for different samples after washing with distilled water and after washing with hydrochloric acid and distilled water. In that figure, the first sample is UAK2-800, which has been prepared using the impregnation method with a 2:1 KOH/anthracite ratio, and a carbonization process at 700°C for 1 h, using a nitrogen flow rate of 800 ml/min and a heating rate of 5°C min. In the next samples, the only variable, which was modified with respect to UAK2-800, is shown. It can be observed that for all the cases, the washing with hydrochloric acid before distilled water produced somewhat higher micropore volumes, except for the sample with the KOH/anthracite ratio of 1:1. In this case, the results obtained after washing with water or with hydrochloric acid and water were the same.

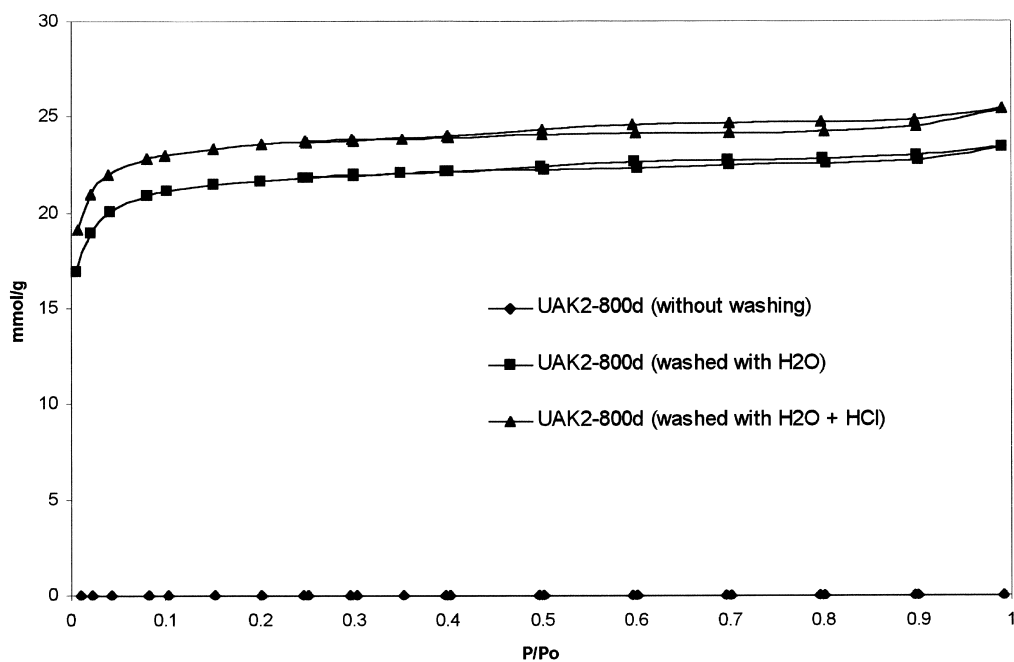


Fig. 5. N₂ adsorption isotherms at 77 K. Effect of the washing step after the pyrolysis process.

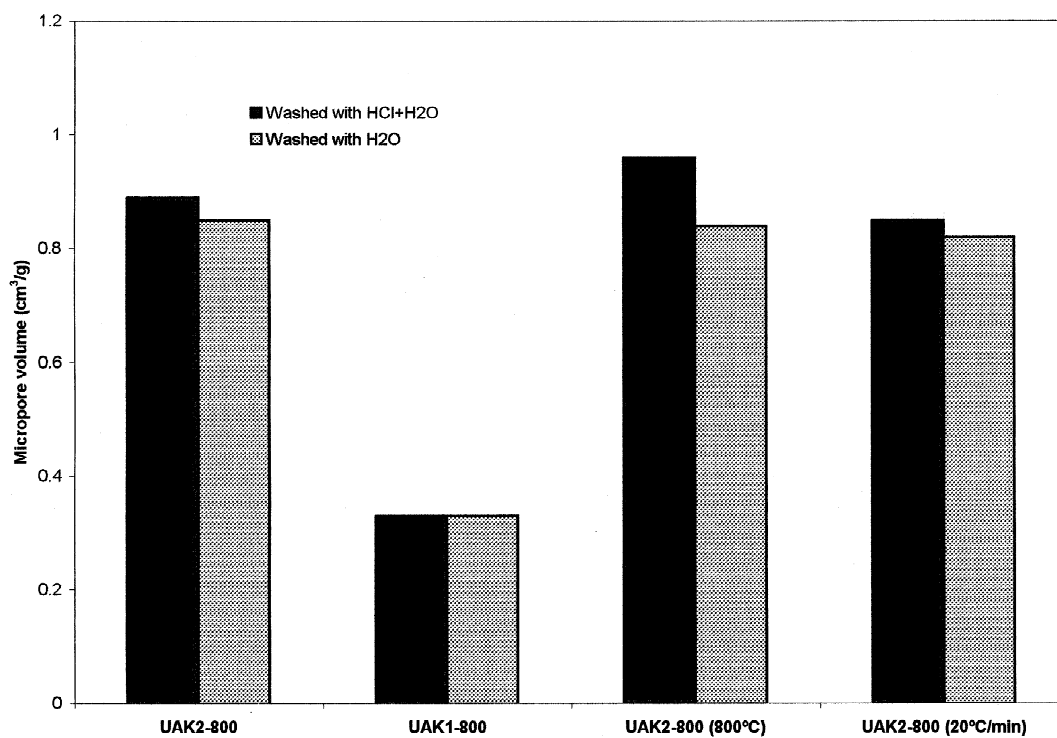


Fig. 6. Micropore volume calculated from N₂ data for different samples washed with water and with water and hydrochloric acid.

4. Conclusions

From the results presented in this study, it can be concluded that the raw material used, Spanish anthracite, is a very good starting material for the preparation of activated carbons in a single stage pyrolysis process. High micropore volume activated carbons (up to $1.45 \text{ cm}^3/\text{g}$) with a quite narrow micropore distribution and BET surface area as large as $3200 \text{ m}^2/\text{g}$ can be prepared from a mixture of this anthracite and KOH. Depending on the final application, the pore volume and surface area of the activated carbon derived from the anthracite can be controlled by choosing suitable activation parameters.

Among all the parameters studied in the present paper, the main factor affecting the final porous texture of the activated carbons is the KOH/anthracite ratio. The higher the KOH/anthracite ratio, the wider the micropore size distribution. However, it has been seen that the micropore volume does not follow that trend but presents a maximum for the KOH/anthracite ratios of 4:1. It has been observed that for KOH and anthracite, the creation of micropores seems to be more important than the opening of those micropores created. Thus, all the activated carbons prepared with different KOH/anthracite ratios are essentially microporous materials.

The present paper introduces the study of nitrogen flow rate, a parameter that hardly ever has been modified in previous studies. The results indicate that nitrogen flow rate has a very important effect on porosity development. It has been shown that a higher nitrogen flow rate during the carbonization process produces activated carbons with a much higher micropore volume. This behaviour is presented by samples prepared using different KOH/anthracite ratios.

Other preparation variables with a direct effect on the final porous texture of the activated carbons are the temperature and time of pyrolysis and the heating rate. As expected from previous results, the higher the temperature and the time of pyrolysis, the higher the micropore volume. In the other way, the lower the heating rate during the pyrolysis process, the higher the microporosity development.

Finally, it can also be concluded that an acid washing could be avoided because the results are not very different from those obtained with water washing. However, in the former case a somewhat higher micropore volume and much lower ash content can be obtained because all the potassium compounds are removed. The effect of the washing step is more important for activated carbons with higher KOH/anthracite ratios.

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