Preparation of active carbons from coal
Part III: Activation of char

J.J. Pis [a,*], M. Mahamud [a], J.A. Pajares [a], J.B. Parra [a], R.C. Bansal [b]

[a] *Instituto Nacional del Carbón, C.S.I.C. Apartado 73, 33080 Oviedo, Spain*
[b] *Department of Chemical Engineering and Technology, Panjab University, Chandigarh, India*

Abstract

Active carbons with a burn-off of 52% have been prepared from four coals of different rank and origin after preoxidation to different degrees at 543 and 473 K, and further carbonization at 1123 K. The activation has been carried out with CO_2 at 1123 K at two flow rates viz. 7 cm^3 min^{-1} and 500 cm^3 min^{-1}. Active carbons have also been prepared from a preoxidized coal by activation to different degrees of burn-off between 10 and 80%. The effect of the degree of oxidation, the flow rate of the activating gas and the extent of burn-off on the porous structure development of active carbons has been examined. The active carbons prepared from unoxidized coal have poor textural characteristics (porosity, N_2 and CO_2 surface area). Nevertheless, the textural characteristics are enhanced as the degree of preoxidation of the coal is increased. The low flow rate of CO_2 (activating gas) produces active carbons with a better microporous character. The degree of activation (the extent of burn-off) of the carbon determines the porous structure of the active carbon. At low degrees of burn-off (less than 50%) the product is largely microporous. At higher degrees of burn-off between 35–65% the product has a mixed porous structure and contains all types of pores. Active carbons with a given textural character can be obtained by controlling the degree of oxidation of coal and the degree of activation of the carbonized material. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Coal oxidation; Coal char; Textural properties; Active carbons

---

* Corresponding author. Tel.: +34-985-28-08-00; fax: +34-985-29-76-62; e-mail: jjpis@muniellos.incar.csic.es

1. Introduction

Coals are increasingly being used as raw materials for the preparation of active carbons because of their low cost and easy availability. The preparation involves three steps namely: oxidation of coal, carbonization into char and char activation. Oxidation and carbonization have been discussed respectively in Part I and Part II of the present series. Activation of the carbonized product will be the subject matter of this paper.

The objective of activation is to increase pore volume and to widen micropores which were produced during carbonization process and to create some new porosity. The activation is generally carried out by two methods: chemical activation and physical activation [1,2]. Chemical activation involves thermal decomposition of the raw material impregnated with certain chemical agents [3–6] while physical activation involves gasification of the char by oxidation with oxygen [7–9], steam [7,10–12] or CO_2 [4–7,12–23]. The active oxygen in the activating agent basically burns away the more reactive portions of the carbon skeleton as CO and CO_2, the extent of burn-off depending upon the nature of the gas employed and the temperature of activation.

The activation takes place in two steps. In the first step it preferentially eliminates disorganized carbon and residual tar material leading to opening of some closed pores. The aromatic sheets are exposed to the action of the activating agents. In the second phase of the reaction, the significant effect is burning of the aromatic ring system and widening of the existing pores or the formation of large sized pores by a complete burn out of the walls between the adjacent pores. This results in an increase of macroporosity and mesoporosity and a decrease in the volume of the micropores.

All the three activating agents, i.e., air, CO_2 or steam produce a different distribution of porosity and this difference becomes more pronounced at high burn-offs [7,8,13,16,21]. While activation with CO_2 develops mainly microporosity over the entire range of burn-offs, activation in steam produces mesoporosity to a higher extent [7]. The activation with air shows a different behaviour. A very low burn-off results in a development of microporosity which changes very little with further burn-offs [8].

In general, the quality of the active carbon obtained or the development of the porous structure by physical activation depends upon the degree of burn-off of the carbon. A lower degree of burn-off generally produces active carbon with a more microporous structure and with a very narrow distribution of pores. With increase in the degree of burn-off, the pores become wider and there is development of substantial amount of meso- and macroporosity.

The present paper discusses the effect of preoxidation of coal, the gas flow rate during activation with CO_2 and the degree of burn-off on the textural development in active carbons.

2. Experimental

Chars obtained by carbonization of preoxidized coals, as described in Parts I and II of this series were used. Chars were gasified with pure CO_2 at 1123 K. A higher activation temperature was not chosen in order to avoid the overlapping of the effects of carbonization (carried out at 1123 K) and the activation process itself. This operation

was carried out in a double jacket quartz reactor which inner tube (i.d. 20 mm) contains the char sample (7 g, particle size 1–3 mm) to be gasified. A porous plate at the bottom, holds the sample and allows the flow of gas through it. The reactor was introduced inside a vertical furnace that by means of a PID controller keeps the temperature at the desired level. A gas chromatograph set-up allows on line evaluation of the degree of burn-off that was more precisely determined gravimetrically. A gas manifold allows sending N_2 through the sample during the heating and cooling periods and also controlling the CO_2 flow rate during the activation time.

Total open pore volume and porosity were obtained from measurements of true (helium) and apparent (mercury under 1 bar pressure) densities. The apparatus used were a Micromeritics 1320 Autopycnometer and a Macropores Unit 120 from Carlo Erba. Specific surface areas and meso- and microporosity were determined from physical adsorption of N_2 at 77 K using the BET method, and physical adsorption of CO_2 at 273 K fitting the data by using the DR method. The experimental sets used were a Micromeritics ASAP 2000 and a Carlo Erba Sorptomatic 1900.

3. Results and discussion

Active carbons with a burn-off of about 52% have been prepared from chars obtained by carbonization of four coals (ML, TU, Q1 and Q2) of different rank and origin preoxidised to different degrees at 543 K and for one coal (ML) at 473 K. The activation has been carried out in CO_2 at 1123 K at two flow rates viz. 7 cm^3 min^{-1} and 500 cm^3 min^{-1}. The time of activation to achieve ∼ 52% burn-off depends upon the nature and the degree of oxidation of the coal and the gas flow rate. For a gas flow rate of 7 cm^3 min^{-1} the time of activation for the unoxidized coal varied between 30–80 h and was reduced to between 20–35 h in case of the preoxidized coals. This is due to an increase in the reactivity of the chars as a result of preoxidation. When the gas flow rate was 500 cm^3 min^{-1} the time of activation was reduced to between 2–9 h.

3.1. Effect of coal preoxidation on the textural development of active carbons

The total pore volume, V_T, calculated from true and apparent densities increases considerably as a consequence of coal preoxidation in all active carbons (Table 1). However, the extent of increase depends upon the nature of the precursor coal and the degree of its oxidation. For a preoxidation of four days at 543 K, the increase in pore volume is about three times in the case of active carbons obtained from ML and TU coal chars while the increase is only about 1.5 times in case of active carbons obtained from Q1 and Q2 chars. It is interesting to note that the ultimate value of the total pore volume of active carbons obtained from different coals after 4 days preoxidation at 543 K is about the same (cf. Table 1). The large increase of V_T in case of ML and TU coal active carbons can be attributed to the smaller value of V_T in case of the active carbons obtained from unoxidized ML and TU coal chars which can, in turn, be attributed to the more plastic nature of these coals (refer to Part I). Similar values of V_T in case of different active carbons, as mentioned above, indicate that after oxidation all the coals

Table 1
Total pore volume and surface areas of active carbons activated with CO_2 to a burn-off of 52% under a flow rate of 7 cm^3 min^{-1}

Oxidation time (days)	Total pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	
		N_2 (BET)	CO_2 (DR)
ML: Preoxidation temperature 543 K			
0	0.285	245	227
1	0.509	908	684
2	0.744	1381	990
3	0.679	1350	992
4	0.761	1427	1087
TU: Preoxidation temperature 543 K			
0	0.211	293	141
1	0.502	766	640
2	0.639	955	738
3	0.748	1095	852
4	0.744	1309	1121
Q1: Preoxidation temperature 543 K			
0	0.486	264	219
2	0.693	1409	714
4	0.776	1588	894
Q2: Preoxidation temperature 543 K			
0	0.679	638	380
2	0.752	1673	786
4	0.771	1621	832
ML: Preoxidation temperature 473 K			
3	0.430	789	572
7	0.526	1066	787
14	0.609	1306	903

attain the same ultimate chemical and porous structure. This is shown by a similar chemical composition of the coals after oxidation for 4 days at 543 K (refer to Part I).

The pore size distribution in different active carbons was obtained from apparent density, mercury porosimetry and adsorption isotherms of N_2 (77 K) and CO_2 (273 K), following the pore size classification proposed by the IUPAC. It is seen that the pore size distribution (Figs. 1 and 2) is strongly influenced by the degree of preoxidation of the coal. The distribution generally becomes more and more favourable to micropores as preoxidation is enhanced, especially at low degrees of preoxidation. The active carbons obtained from unoxidized coal chars show a microporosity of less than 60% which increase to more than 80% after 2 days preoxidation at 543 K (cf. Fig. 1) and 7 days preoxidation at 473 K (Fig. 2). There is a corresponding decrease in the number of macropores. The production of mesoporosity is only slight.
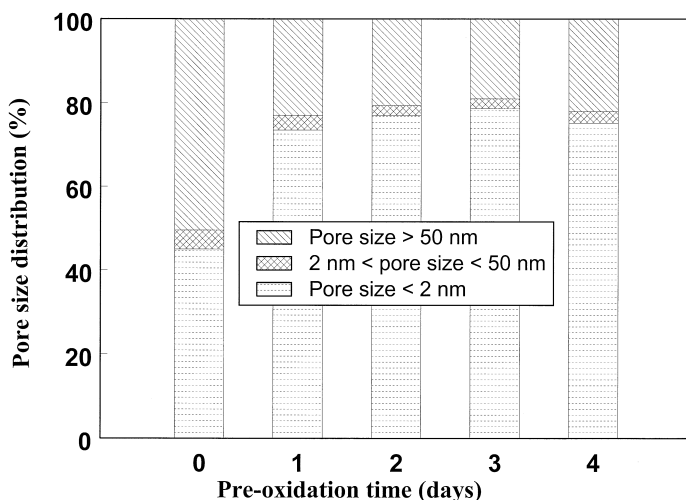
Fig. 1. Pore size distribution of active carbons obtained from ML chars. CO_2 gasification at 1123 K with a flow rate of 7 cm^3 min^{-1}. Temperature of coal preoxidation: 543 K.

Both the CO_2 (DR) and the N_2 (BET) surface areas of active carbons (Table 1) increase with increasing the degree of preoxidation of the coal. The increase, however, depends upon the nature of the coal. It is interesting to note that the maximum increase in surface area takes place during the first 2 days of preoxidation, further oxidation resulting comparatively in smaller changes in most cases. It appears that the coal, after this initial oxidation attains more or less a definite porous structure.

It is also seen (cf. Table 1) that while the CO_2 surface areas of active carbons obtained from Q1 and Q2 coal chars are considerably smaller than those obtained from
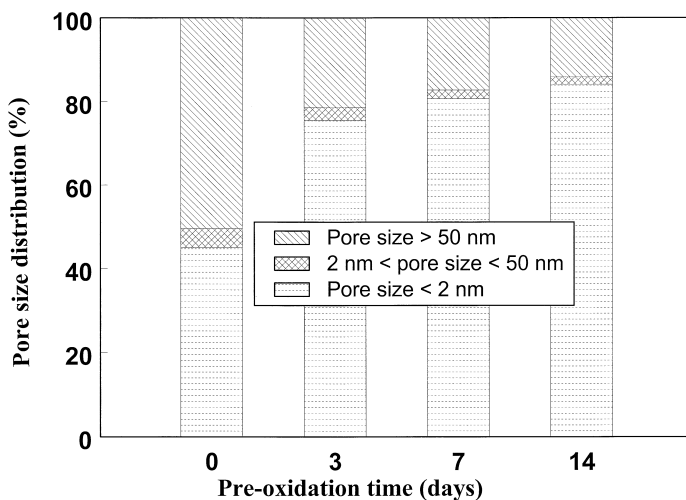

Fig. 2. Pore size distribution of active carbons obtained from ML chars. CO_2 gasification at 1123 K with a flow rate of 7 cm^3 min^{-1}. Temperature of coal preoxidation: 473 K.

ML and TU coal chars for the same period of preoxidation (4 days), the N_2 surface areas are larger in the case of Q1 and Q2 coal active carbons. This is despite the fact that the textural developments in the chars obtained from Q1 and Q2 coals were inferior to those in ML and TU coal chars. A possible explanation would be that a considerable part of the pore volume in chars Q_1 and Q_2 may have remained hidden in the form of closed inaccessible pores. This hidden pore volume is revealed only after the gasification of the char, indicating that the gasification of the char results in opening closed porosity. In addition, the Q1 and Q2 chars are much less reactive than ML and TU chars as shown by the semireaction time (the time necessary for attaining a conversion of 50%). These values for semireaction time are between 20–45 h in case of ML and TU coal chars and between 35–75 h for Q1 and Q2 coal chars.

3.2. Effect of gas flow rate on the textural characteristics of active carbons

In order to explain the effect of the activating gas flow rate on the development of the textural character in active carbons, chars obtained from ML and TU coals were activated with CO_2 at two flow rates, i.e., 7 cm³ min^{-1} and 500 cm³ min^{-1} to a constant burn-off of around 52%. It was found that the time of activation was about five times higher when gasification is carried out at the lower flow rate. This provides a larger residence time for the activating gas favouring a more extended molecular rearrangement and a consequent increase in true density. The lower flow rate of CO_2 also results in the formation of larger amounts of CO which inhibits the gasification rate so that it takes place more uniformly through the whole carbon particle network and creates more open porosity.

The higher flow rate does not imply a deeper penetration of the activating gas into the internal microporosity but rather it implies an increased burn-off of the external part of the carbon particle. Therefore, at higher flow rates, the loss of the external surface of the particle becomes more important than the generation of internal porosity. Thus, a more porous carbon material is obtained when the rate of CO_2 is lower (cf. Fig. 3).
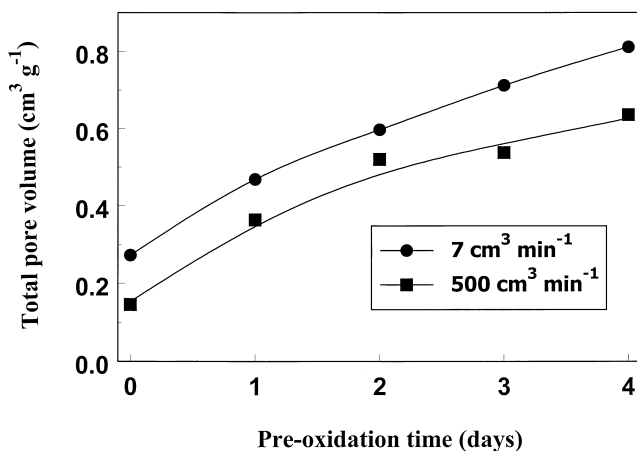

Fig. 3. Evolution of the total pore volume of active carbons obtained by CO_2 gasification of TU chars at 1123 K and ∼ 52% burn-off.
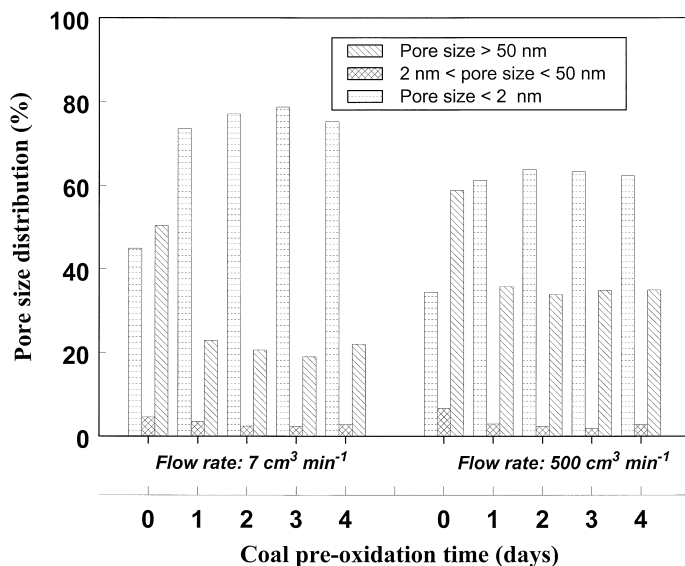
Fig. 4. Pore size distribution of active carbons obtained by CO_2 gasification of ML chars at 1123 K and $\sim 52\%$ burn-off, activated at different flow rates.

The flow rate of CO_2 also influences the pore size distribution in active carbons (Fig. 4). The formation of micropores is more important at low flow rates because the more uniform gasification develops better the microporous character of the pores. At higher flow rates while the total pore volume is less, the percentage of macropores is larger (Fig. 4). The CO_2 (DR) and N_2 (BET) surface areas are usually larger when the flow rate is lower. However, the large difference occurs in the case of N_2 surface areas, the CO_2 surface areas differing only slightly. For instance, the N_2 surface area of the active carbon obtained from 4 day preoxidised ML coal char has a value of 1427 m^2 g^{-1} when activated at the lower flow rate compared to 1107 m^2 g^{-1} when activated at the higher flow rate.

3.3. Effect of burn-off on the development of textural characteristics in active carbons

Chars obtained from ML coal preoxidized for 2 days at 543 K and for 7 days at 473 K were activated in CO_2 at 1123 K with a gas flow rate of 7 cm^3 min^{-1} to burn-offs between about 10 and 80% and their true and apparent densities, total pore volume, porosity and CO_2 (DR) and N_2 (BET) surface areas were determined. It was found that the true density increases slightly with increasing the burn-off for the active carbons prepared by both preoxidation treatments, while the apparent density continuously decreases. Such an increase in true density has been observed by several workers [16,22] and has been attributed to the opening of some closed porosity during the initial gasification process.

The total pore volume V_T (as calculated from true and apparent densities) and the porosity (cf. Table 2) increase continuously with increasing burn-off. The increase in

Table 2
Total pore volume, porosity and surface area of active carbons obtained from ML char after activation to different degrees of burn-off

Burn-off (%)	Total pore volume (cm^3 g^{-1})	Porosity (%)	Surface area (m^2 g^{-1})	
			N$_2$ (BET)	CO$_2$ (DR)
Preoxidation time: 2 days at 543 K				
0	0.252	0.321	402	518
13	0.305	0.374	622	654
34	0.468	0.490	1012	943
56	0.743	0.609	1381	990
64	0.835	0.641	1656	1037
79	1.229	0.725	1932	961
Preoxidation time: 7 days at 473 K				
0	0.174	0.239	105	446
14	0.223	0.298	372	481
32	0.301	0.371	544	636
51	0.526	0.521	1066	787
62	0.543	0.523	1025	805
75	0.776	0.617	1321	761

pore volume at 80% burn-off is more than four times the pore volume of the unactivated char. The percentage distribution of microporosity (cf. Fig. 5) increases with the degree of gasification up to about 35% of burn-off. The distribution of micro and macropores remains more or less constant in the burn-off range of 35–65% except that a small amount of mesoporosity is created. At higher degrees of burn-off, some of the
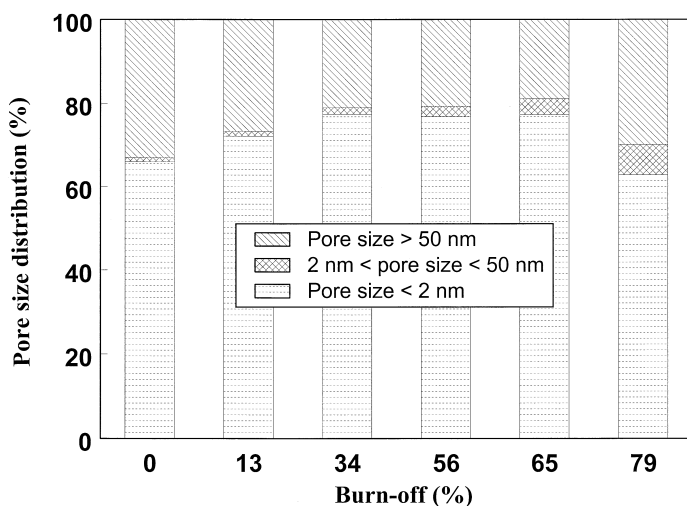

Fig. 5. Evolution of pore size distribution with burn-off of active carbons obtained by CO$_2$ gasification of ML chars at 1123 K. Coal preoxidation: 2 days at 543 K.

micropores are converted into meso- and macropores. The creation of mesoporosity on gasification is important because it was almost non-existent in chars.

Fig. 6 shows N_2 adsorption isotherms, carried out at 77 K, for the activated materials obtained at different degrees of burn-off. A significant increase in micropore volume can be observed as a consequence of gasification. An opening of the knee of the isotherms was produced as a consequence of the widening of the micropores. A slight increase in the slope of the plateau can also be observed. Both the shape of the isotherm and the changes in the slope indicate that bigger pores were produced at higher burn-off levels. These results agree with those of other authors, who observed that during progressive gasification of the char some pore enlargement and, therefore, a shift from microporosity to mesoporosity occurs [23].

The development of CO_2 and N_2 surface areas with the degree of burn-off is shown in Table 2. At lower degrees of burn-off (up to 20%) the CO_2 surface area is larger than the nitrogen surface area indicating a relatively high microporous character of the activated carbon at this low degree of burn-off. As the degree of burn-off is increased, both the CO_2 and nitrogen surface areas increase, but the increase in N_2 surface area is much bigger. The CO_2 surface area reaches a maximum and remains more or less constant when the degree of burn-off is between 35–65% and then shows a slight decrease at higher degrees of burn-off. The nitrogen (BET) surface area, on the other hand, increases almost linearly with the degree of burn-off and the values are much larger compared to those of the CO_2 surface areas at a given degree of burn-off. Lower N_2 surface area at lower degrees of burn-off can be due to the presence of very fine micropores which are inaccessible to nitrogen at 77 K, probably due to activated diffusion effects [8]. The increase in the degree of burn-off results in widening of the
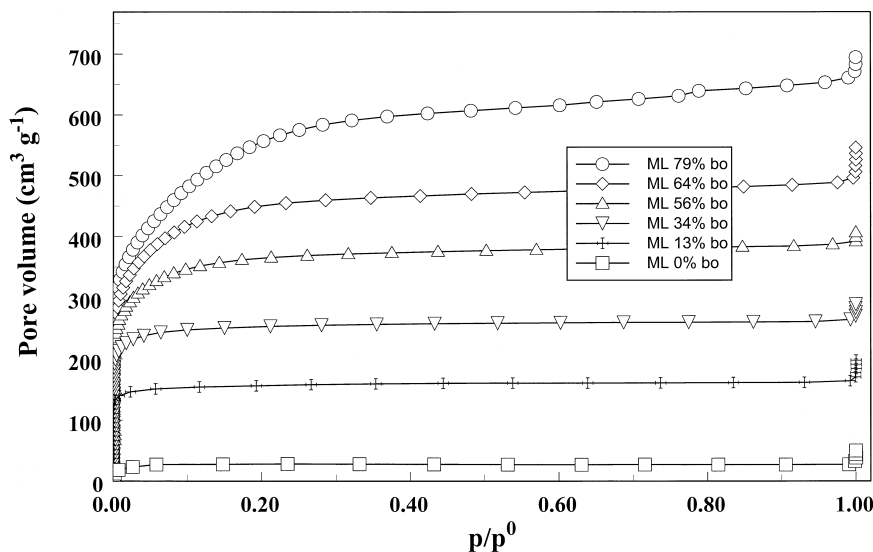

Fig. 6. N_2 adsorption isotherms at 77 K of active carbons obtained by CO_2 gasification of ML chars at 1123 K at different burn-off. Coal preoxidation: 2 days at 543 K.

micropores so that more and more of these are now available for the adsorption of nitrogen. The distribution of porosity into micro, meso- and macropores (Fig. 5) supports this observation. The distribution of porosity also explains the constancy of the CO_2 surface area in the range of 35–65% burn-off and a subsequent decrease at higher degrees of burn-off. The results presented in this paper and elsewhere [13,16,22,23] show that a microporous active carbon is produced when the degree of burn-off is less than about 50% and a more macroporous character of the active carbon when the degree of burn-off is greater than about 80%. When the degree of burn-off is between 50–80%, the product has a mixed porous structure and contains all types of pores.

3.4. The importance of coal preoxidation on the pore structure development of active carbons

It appears from the results presented in this paper and in Parts I and II of the present series that the pore structure development in active carbons from coals has to be considered under three steps: oxidation, carbonization and activation. Figs. 7–9 present the development in porosity and CO_2 (DR) and N_2 (BET) surface areas as a function of the degree of oxidation of the coal. It appears that the oxidation of coal is the fundamental and most important step because the active carbons obtained from unoxidized coals have very poor textural characteristics. The oxidation of coal eliminates plastic properties and inhibits the formation of an anisotropic material which has a less developed porous structure. The oxidation also initiates devolatilization resulting in preferential elimination of aliphatic and disorganised carbon and tar material leading to the opening of closed porosity. Consequently the porosity increases, the extent of increase depending upon the degree of oxidation of the coal. Both N_2 (BET) and CO_2 (DR) surface areas increase, but the increase in CO_2 surface area is much larger than the increase in BET surface area which remains almost insignificant. This indicates that the oxidized coal contains only narrow microporosity inaccessible to nitrogen molecules at
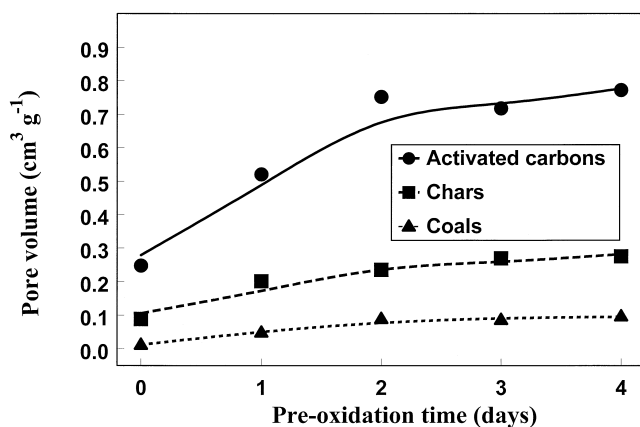

Fig. 7. Modification of pore volume in the coal–char–active carbon series as a consequence of coal preoxidation, using ML coal as precursor material.
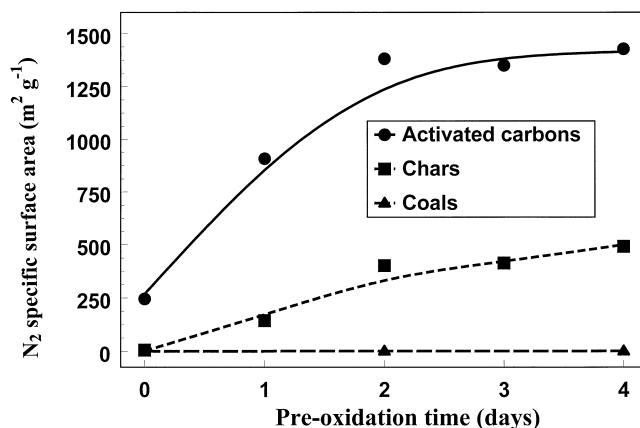
Fig. 8. Modification of N_2 specific surface area in the coal–char–active carbon series as a consequence of coal preoxidation, using ML coal as precursor material.

77 K. Since the oxidation does not involve much of gasification, it starts the cleaning of the micropores and lays the foundation for the development of a primary pore structure.

The carbonisation of the oxidized coal involves thermal decomposition of the coal material, eliminating volatiles and producing a fixed carbon mass and extending the primary pore structure. The pore network created during preoxidation helps in the early release of volatiles during the carbonization step and this inhibits the aromatization reactions. The preexistence of this pore network also facilitates the passage of the gas into the pore body resulting in the development of char porosity with smaller number of closed pores.
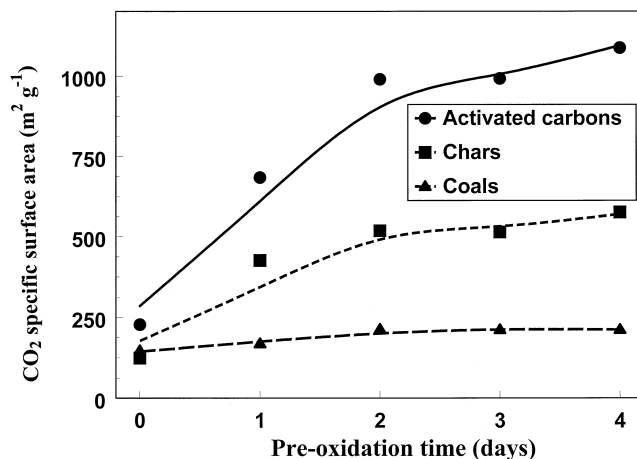

Fig. 9. Modification of CO_2 specific surface area in the coal–char–active carbon series as a consequence of coal preoxidation, using ML coal as precursor material.

The activation process enlarges the diameter of the pores which were created during the carbonization process and creates some new porosity by opening some closed pores. During the first phase, the activation removes disorganized carbon exposing the aromatic sheets to the action of the activating gas and leading to the development of a microporous structure. In the later phases of the reaction, the significant effect is the widening of the existing pores and the formation of large sized pores by a complete burn out of the walls between the adjacent pores. This results in an increase in meso- and macroporosity and a decrease in microporosity. Thus the extent of burn-off of the carbon material is a measure of the degree of activation.

4. Conclusions

The flow rate of the activating gas (CO_2) influences the pore size distribution of active carbons, the formation of micropores being more relevant at low flow rates. This can be attributed to the more uniform gasification achieved when lower flow rates are used. At lower degrees of burn-off the active carbons obtained have a highly microporous character. At intermediate degrees of burn-off, between about 45 and 65%, the active carbons have a mixed porous structure and contain all types of pores. At higher degrees of burn-off, some of the micropores are converted into meso- and macropores, the development of mesoporosity occurring especially in active carbons obtained from preoxidized coals. From the results obtained in the coal oxidation–carbonization–activation sequence it can be concluded that preoxidation of coal is the fundamental and most important step mainly because active carbons obtained from unoxidized coals have very poor textural characteristics. Thus active carbons with a tailor made textural character can be obtained from coal by controlling the degree of preoxidation of the coal, the flow rate of the activating gas and the degree of burn-off of the char.

References

[1] R.C. Bansal, J.B. Donnet, F. Stoeckli, Active Carbon, Marcel Dekker, New York, 1988.
[2] H. Jankowska, A. Swiatkowski, J. Choma, Active Carbon, Ellis Horwood, London, 1991.
[3] M. Jagtoyen, F. Derbyshire, W. Glasser, 21st Bienn. Conf. on Carbon, State Univ. of New York at Buffalo, Extended Abstracts and Program, 1993, p. 414.
[4] F. Rodriguez-Reinoso, M. Molina-Sabio, Carbon 30 (1992) 1111.
[5] J. Laine, S. Yunes, Carbon 30 (1992) 601.
[6] F. Kraehenbuehl, F. Stoeckli, A. Addoum, P. Ehrburger, J.B. Donnet, Carbon 24 (1986) 483.
[7] K. Tomkow, T. Siemieniewka, F. Czeckowki, A. Jankowska, Fuel 56 (1977) 121.

[8] F. Rodríguez-Reinoso, A. Linares-Solano, J.M. Martín-Martínez, J.D. López-González, Carbon 22 (1984) 123.

[9] P. González-Vílchez, A. Linares-Solano, J.A. López-González, F. Rodríguez-Reinoso, Carbon 17 (1979) 441.

[10] J.C. de Sousa, J.B. Parra, J.A. Pajares, J.J. Pis, in: Studies in Surface Science and Catalysis, Vol. 87, Elsevier, Amsterdam, 1994, pp. 603–612.

[11] E. Klose, M. Born, Fuel 64 (1985) 1313.

[12] H. Kühl, M.M. Kashani-Motlagh, H.J. Mühlen, K.H. van Heek, Fuel 71 (1992) 879.

[13] M.J. Muñoz-Guillena, Illán-Gómez, J.M. Martín-Martínez, A. Linares-Solano, S.-M. de Lecea, Energy and Fuels 6 (1992) 9.

[14] B. Mc Enaney, N. Dovaston, Carbon 13 (1975) 515.

[15] V.M. Kalback, L.F. Brown, R.E. Wert, Carbon 8 (1970) 117.

[16] M.C. Mittelmeijer-Hazeleger, J.N. Martín-Martínez, Carbon 30 (1992) 695.

[17] J.C. de Sousa, M. Mahamud, J.B. Parra, J.J. Pis, J.A. Pajares, Fuel Process. Technol. 36 (1993) 333.

[18] J.A. Pajares, J.J. Pis, A.B. Fuertes, A.J. Pérez, M. Mahamud, J.B. Parra, in: F. Rodríghez-Reinoso et al. (Eds.), in Studies Surface Science and Catalysis, Vol. 62, Elsevier, Amsterdam, 1991, pp. 347–355.

[19] B. Ruiz, J.B. Parra, T. Alvarez, A.B. Fuertes, J.A. Pajares, J.J. Pis, Applied Catalysis A: General 98 (1993) 115.

[20] J.A. Pajares, J.J. Pis, A.B. Fuertes, J.B. Parra, M. Mahamud, A.J. Pérez, in: G. Poncelet et al. (Eds.), Preparation of Catalysts V, Elsevier, Amsterdam, 1991, pp. 439–448.

[21] H. Marsh, B. Rand, Carbon 9 (1971) 47.

[22] M. Kawahata, P.L. Walker Jr., Proc. of the 5th Carbon Conf., Vol. 2, Pergamon, New York, 1963, p. 251.

[23] F. Rodríguez-Reinoso, in: J. Lahaye, P. Ehrburger (Eds.), A Fundamental Issues in Control of Carbon Gasification Reactivity, Klumer, Amsterdam, 1991, pp. 533–571.