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Carbon molecular sieves for the concentration of oxygen from air

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The micropore structure of a number of American coals varying in rank from LVB to lignite has been modified by two methods: (1) heat treatment in nitrogen to 800–900°C, and (2) air oxidation near the ignition temperature followed by heat treatment to 900–1000°C in nitrogen. The second method of treatment is a necessity for coking coals. The chars from HVC coal using method (1) and from LVB coal using method (2) showed selective oxygen adsorption from air. Preferential oxygen uptake is attributed to an initial rate of oxygen adsorption that is higher than that for nitrogen owing to molecular sieve structure. Carbons obtained from coconut shells and some highly crosslinked synthetic polymers (for example, polydivinyl benzene) also showed selective oxygen adsorption. Adsorption of both gases on these carbons is primarily physical, that is, adsorption and desorption cycles can be performed by pressure swing with no significant loss of capacity. The slope of the oxygen isotherm is higher than that of the nitrogen isotherm, indicating that oxygen adsorption is enhanced over that of nitrogen at higher pressures. Operating at pressures around 6·3 MPa and 25°C with air, oxygen concentration in the desorption product stream can be increased to about 36%. Using three beds of carbon in series, the final product gas can be concentrated to about 80% oxygen. The fraction, by volume, of the inlet gas which is realized as product gas depends upon a number of variables.

Oxygen is being used in large tonnages in different technological processes. Initially, oxy-acetylene welding was the primary outlet for oxygen but increasingly higher quantities are being used in steel making, sewage treatment, and coal-gasification processes; and when additional coal-gasification processes now in the pilot-plant stages attain commercial operation the demand will increase many fold. The established method of separating oxygen from air involves drying, compressing, cooling to low temperature and fractional distillation. Separation or preliminary concentration of air by selective adsorption at or near room temperature appears to be an interesting alternative approach. A method and apparatus for increasing the oxygen content of air by using a heatless fractionation technique was described by Skarstrom[1]. The adsorbent used was Type X zeolite which selectively adsorbs nitrogen.

Coals are porous bodies; a fraction of their pores have diameters similar in size to those of simple molecules as shown by Anderson *et al*[2] among others, and that coal behaves as a molecular sieve. Some coals adsorb[2] larger amounts of butane than of isobutane under equivalent conditions. The nature of the porosity in a large number of American coals was investigated by Gan *et al*[3]. Coals have a wide distribution in pore sizes ranging from about 3000 nm to about 0·5 nm. The size distribution and the total open-pore volume depends on coal rank. Raw coals will not be efficient molecular sieves because the pore volume which is accessible through apertures of molecular size is limited. Also raw coals are not chemically stable. However, the pore structure of coal can be modified by heat treatment and the distribution of pore sizes made narrower. Heat treatment at the same time will bring about chemical stability in the resulting coke or char. A process for the partial separation of oxygen from air using some natural coals and oxidized, heat-treated coals has been described in a number of patents[4].

The oxygen molecule has a kinetic diameter of 346 pm calculated from the minimum equilibrium cross-sectional diameter[5]. By comparison, nitrogen has a kinetic diameter of 364 pm [5]. A truly selective adsorbent is required to have its critical pore diameter intermediate between the two values mentioned above. It will be difficult if not impossible to make an adsorbent with a unidisperse pore system from a complex amorphous material like coal. Therefore, a complete separation of oxygen from nitrogen by a single adsorption step on a coal-based carbon is not expected. It is hoped that a microporous material can be developed that will impose greater resistance to nitrogen adsorption compared to that of oxygen. By adjusting the process variables, that is time, pressure, and temperature for adsorption, the uptake of nitrogen from an air stream will be minimized, thereby producing a much higher concentration of oxygen in the adsorbed phase. When the adsorbed gases are collected by reduction of pressure, the desorbed gases will be richer in oxygen compared with the content in air.

The way the change in the pore structure of coals brings about selectivity in physical adsorption is the main subject of this study. Carbons produced from synthetic polymers and coconut shell have been used for comparative purposes.

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Table 1 Coal analyses

PSOC sample	ASTM rank	Ash (%)	Ultimate analysis (% daf)				
			C	H	N	S	O
127	Low-vol. bit.	7·0	89·4	4·7	0·92	1·1	3·9
35	Med.-vol. bit.	4·9	88·5	4·9	0·25	0·65	5·7
171	HVA bit.	7·5	82·5	5·6	1·3	3·35	7·3
212	HVC bit.	2·6	79·2	5·4	1·4	0·85	13·2
181	Sub. bit. A	7·8	77·5	5·1	1·0	0·63	15·8
190	Sub. bit. B	8·4	75·8	5·3	1·0	3·3	14·6
138	Lignite	10·2	74·4	4·9	0·37	0·75	19·6
91	Lignite	7·7	70·8	4·8	0·81	0·41	23·2

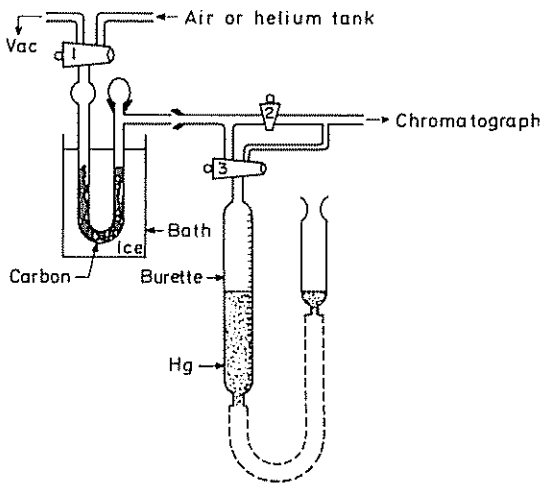


Figure 1 Atmospheric-pressure apparatus for measuring possible selective uptake of oxygen from air

EXPERIMENTAL

Carbon precursors used

Analyses of the coals used are shown in *Table 1*. A number of carbons from synthetic polymers prepared earlier[6,7] have also been used. Two special carbons (Carbosieve-B and MSC-V), a commercial active carbon (CXC), and a sample of 4A zeolite in 1·6 mm (1/16 in) pellet form were also used. These samples were obtained from Supelco, Inc., Pittsburgh Activated Carbon Company, Columbia Carbon Company, and Union Carbide Corporation, respectively. Carbosieve-B is used as a chromatographic packing. MSC-V is recommended for some molecular-sieving applications. Two samples of carbon have been prepared from coconut shell.

Heat treatment

Non-coking coals were heat-treated in a fluidized bed in a nitrogen atmosphere, using a heating rate of 5°C/min and a soak time of 2 h at maximum temperature. Coking coals were heated in a horizontal tube furnace, with nitrogen flowing over the static bed. The rate of heating and soak time were the same as used in the fluidized bed. The coke mass was ground before adsorption runs, with a 40 X 70 mesh (Tyler) particle size used unless indicated otherwise.

Dried pieces of coconut shell were held in a silica boat nd heated at 5°C/min to 500°C in a stream of nitrogen. After this the char was crushed and sieved, and a 20 X 40-mesh fraction was heat-treated at higher temperatures in the fluidized bed, using the same operating conditions as for the non-coking coals.

Low-temperature oxidation

Partial oxidation of selected samples was carried out at 150–250°C for different lengths of time in the fluidized bed using air as the oxidant. Low temperatures (below critical oxidation or ignition temperature) and fluidized-bed operation were used to obtain uniform oxidation throughout the coal particles. Oxidative treatment removed coking properties when the coals were further heat-treated at higher temperatures in the fluidized bed.

Surface-area measurement

Nitrogen and carbon dioxide surface areas were measured using a volumetric apparatus[3]. Samples were outgassed overnight at 150°C prior to adsorption measurements. Nitrogen areas were calculated from adsorption data taken at −195°C using the BET equation and carbon dioxide areas were calculated from adsorption data taken at 25°C using the Dubinin–Polanyi equation[3].

Adsorption of nitrogen and oxygen

Isotherms and rates of adsorption of nitrogen and oxygen were determined in the same volumetric apparatus used for surface-area measurements. Five minutes were allowed for each adsorption point. The following sequence of steps was followed. Carbon samples were degassed at 150°C for 8 h under high vacuum before adsorption. The first isotherm determined in the case of carbons was that of nitrogen. The sample was then degassed for 30 min at the adsorption temperature, and the first oxygen isotherm, O_2 (I), was determined. Oxygen adsorption was then repeated after allowing another 30 min degassing at the same temperature, giving O_2 (II). For the zeolite sample the initial degassing temperature was 300°C. The rates of adsorption of oxygen and nitrogen were measured at a constant pressure of 26·6 kPa at 25°C for a number of samples.

Measurement of selective adsorption of oxygen

Atmospheric pressure apparatus. For measuring selective adsorption of oxygen from air, the following experimental arrangement was used. The principal features of the apparatus are shown in *Figure 1*. 15 g of carbon were taken in the

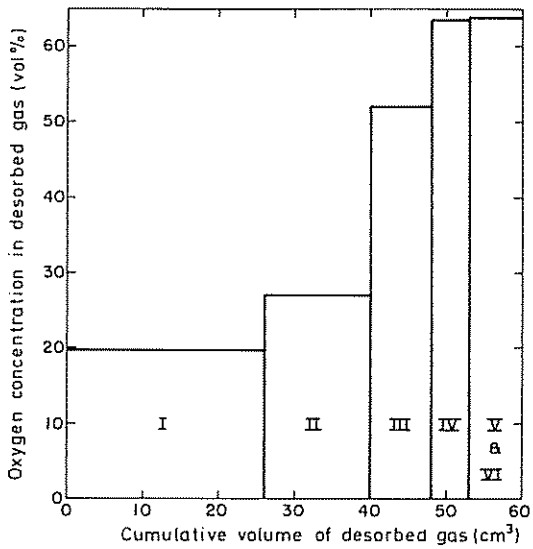


Figure 2 Volume and oxygen content of gas recovered for successive desorption steps at 0°C following the passage of air through a bed of coconut char (sample 38) at 0°C. Exact procedure described in text

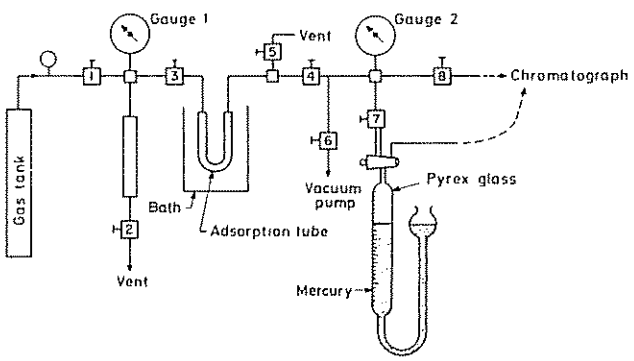


Figure 3 Elevated-pressure apparatus for measuring possible selective uptake of oxygen from air

U-tube placed in an ice bath. The sample was degassed at 0°C and then helium was introduced to fill up the U-tube to atmospheric pressure. Air was then introduced at 15 cm^3 (STP)/min through stopcock 1. Stopcock 3, connecting the burette, was kept closed. The effluent gases coming through stopcock 2 passed through the sampling valve of a chromatograph (Fisher Gas Partitioner). The time required for a single analysis was 1·5 min and so samples of the effluent could be analysed at intervals of 2 min. When the oxygen concentration in the effluent approached 20%, by volume, the flow of air was stopped by closing stopcock 1. Stopcock 2 was closed at the same time. Depending on the type of carbon, the time for an adsorption run was in the range 12 to 20 min. The gas remaining in the system was then collected in the calibrated burette by opening stopcock 3. The burette with the mercury reservoir could be operated like a piston pump. The gas was collected for a number of strokes until less than 2 cm^3 of gas were collected per stroke. The amount of gas collected in the burette in the first step (stroke) consisted primarily of the gas remaining in the free space of the adsorption system. A time of 30 s was allowed for each desorption step. Amounts of gas collected in each desorption step were measured and analysed. Results for a typical run are illustrated in *Figure 2* for coconut char, 20 X 40 mesh, heat-treated to 950°C. The time of the run which elapsed before desorption was started was 17 min. The gas obtained in the first desorption step contained only 19·6% O_2 by volume, that is the gas contained less oxygen than normal air. The gas obtained in subsequent steps was richer in oxygen, the concentration in the gas obtained in the last step being 63·6% by volume. For the purpose of reporting the data, the cumulative volume of gas obtained from the second to the last step is termed desorbed gas. In this particular experiment, 2·04 cm^3 (STP)/g of desorbed gas of 45·8% O_2 content was obtained.

Adsorption runs were made with different carbons under similar conditions and the performance of the carbons was compared on the basis of the amount of gas desorbed and its oxygen content. A number of adsorption and desorption cycles were performed for each sample. Reproducible values of the desorbed-gas parameter were found if 10 min degassing time under vacuum at adsorption temperature was allowed between cycles.

Pressure sorption apparatus. To investigate the effect of pressure on oxygen enrichment and also to study other process variables in a batch operation, a pressure-sorption apparatus, shown in *Figure 3*, was used. The apparatus was built of stainless-steel tubing and high-pressure valves, except for the Pyrex glass burette. The pressure indicators were two Bourdon gauges. Different sections of the apparatus were calibrated with air using the Pyrex glass burette. Two adsorption temperatures, 0°C and 25°C, were used. The inflowing gas for most of the runs was air, but a number of runs were made using gas mixtures of higher oxygen concentration. During a run (adsorption and desorption), the temperature of the carbon was not altered, that is desorption was completed by the reduction of pressure alone. The maximum pressure used in these runs was about 7 MPa. The sample of carbon (15 g), previously dried at 105°C in an air oven, was degassed at adsorption temperature using a rotary oil pump (pressure about 13 Pa absolute) for 30 min. A known quantity of gas was taken in the space between valves 1, 2 and 3. The gas was then admitted to the carbon sample by quickly opening valve 3, keeping valves 5 and 4 closed. A time of adsorption between 0·5 and 7 min was allowed, after which the pressure was reduced in about 0·5 min to a low value (140 to 700 kPa), by opening valve 5*. Valves 3 and 5 were closed and the gas remaining in the system was collected and analysed. The lowest pressure used for desorption was about 14 kPa. After completion of the gas collection, the carbon sample was degassed for 10 min (pressure about 13 Pa) before starting another run. Reproducible results were obtained in different runs with the same sample, that is the capacity remained unaltered if the sample was degassed for 10 min between runs.

RESULTS AND DISCUSSION

Surface area of coals on heat treatment

Changes in pore structure of coals due to heat treatment can be followed by measuring surface-area development. *Table 2* presents nitrogen and carbon dioxide surface areas for two coals heat treated in nitrogen to different temperatures[8]. The carbon dioxide area is regarded as the nearest approach to the true micropore area[9]. The kinetic diameter of carbon dioxide is 330 pm [5]. It is a linear molecule and

* The gas that was released out of the system at this stage would be richer in nitrogen. This gas was not analysed

may orient itself in narrow pore spaces of an adsorbent with its longer dimension parallel to pore length by losing some rotational degree of freedom. Under this particular configuration, the critical size of the molecule is close to that of the oxygen molecule (346 pm). It may be argued, therefore, that the major fraction of the pore area available to carbon dioxide at 25°C will also be available to oxygen (at the same temperature), but may not be available to the slightly larger nitrogen molecule. Nitrogen areas presented in *Table 2* are calculated from adsorption at −195°C. It will be seen that a carbon having a high carbon dioxide area but a low nitrogen area is a necessary but not a sufficient requirement for assuring preferential oxygen adsorption from air.

It is seen from *Table 2* that both areas for the two samples increase following heat treatment at intermediate temperatures. In the case of the HVA sample the carbon dioxide area drops sharply at 800°C, whereas for the lignite sample this parameter remains high up to 900°C. The carbon dioxide area shows some decrease only on reaching 1000°C, that is the microporosity developed remains stable to relatively high temperatures. The nitrogen area of the lignite char also remains high following heat treatment up to 900°C but falls off sharply following treatment at 1000°C. It will be seen that the 1000°C lignite char exhibits selective oxygen adsorption and a high capacity.

Chars produced at 600 and 700°C from the HVA coal PSOC-171 also show major differences in carbon dioxide and nitrogen surface areas while retaining an acceptably high value for carbon dioxide adsorption; and, therefore, might be considered good candidates for molecular sieving. However, as will be seen, a significant fraction of oxygen adsorbed on coal char produced below 800°C is irreversibly held, so that the reversible oxygen adsorption is only about equal to nitrogen adsorption.

Table 2 Surface areas of chars produced by heat treatment of selected coals

Temperature of heat treatment (°C)	Surface area (m^2/g)	
	Nitrogen	Carbon dioxide
	PSOC-171	
0	<1·0	185
600	1·5	400
700	1·0	400
800	0·8	196
900	0·5	38
	PSOC-138	
0	2·2	225
600	266	670
700	107	633
800	116	606
900	113	680
1000	13	528

Adsorption of oxygen and nitrogen

Oxygen and nitrogen isotherms at 25°C were determined for a large number of samples. For the purpose of reporting, the samples are divided into two groups. In the first group belong samples produced previously in this laboratory and commercial samples, and in the second group belong samples prepared during this investigation. Because an arbitrary time (5 min) was allowed for each adsorption point, isotherms do not represent equilibrium values. The volume of gas adsorbed at 79·8 kPa is tabulated for the purpose of comparing the performance of different carbons. All gas volumes are reported at standard temperature (0°C) and pressure conditions (101·3 kPa (760 torr)) through the paper.

Adsorption data on the first group of samples. Adsorption data for these carbons, on a dry basis, are presented in *Table 3*. It is seen that the carbons produced from divinyl benzene and furfuryl alcohol–formaldehyde polymers heat-treated at or above 800°C show higher oxygen adsorption (reversible) compared with that of nitrogen. On carbons

Table 3 Adsorption of oxygen and nitrogen by different carbons

Sample No.	Sample description	Heat-treatment temp. (°C)	CO_2 area (m^2/g)	Adsorption at 25°C and 79·8 kPa (cm^3/g)		
				N_2	O_2(I)	O_2(II)
1	Phenol–formaldehyde[6]	900	520	2·4	2·8	2·8
2	Divinylbenzene[6]	700	443	6·0	7·3	6·8
3	Divinylbenzene[6]	775	378	2·5	5·7	5·3
4	Divinylbenzene[6]	850	394	1·5	2·9	3·1
5	Furfuryl alcohol–formaldehyde[6]	600	428	4·6	5·2	4·6
6	Furfuryl alcohol–formaldehyde[6]	700	390	4·8	6·2	5·2
7	Furfuryl alcohol–formaldehyde[6]	800	414	3·9	6·3	6·1
8	Furfuryl alcohol[6]	750	385	5·9	6·0	5·9
9	Furfuryl alcohol[6]	800	400	6·1	6·1	6·0
10	Vinylidene chloride[7]	1300	1150	9·5	8·6	8·6
11	Vinylidene chloride[7]	1500	1025	6·4	5·8	5·7
12	Saran 489[7]	1000	925	8·1	7·5	7·6
13	Carbosieve B	–	1250	13·3	11·1	11·2
14	MSC-V	–	–	6·2	6·2	6·1
5	CXC	–	1400	4·9	4·9	4·8
16	4A zeolite[5]	–	480	4·7	1·7	1·7

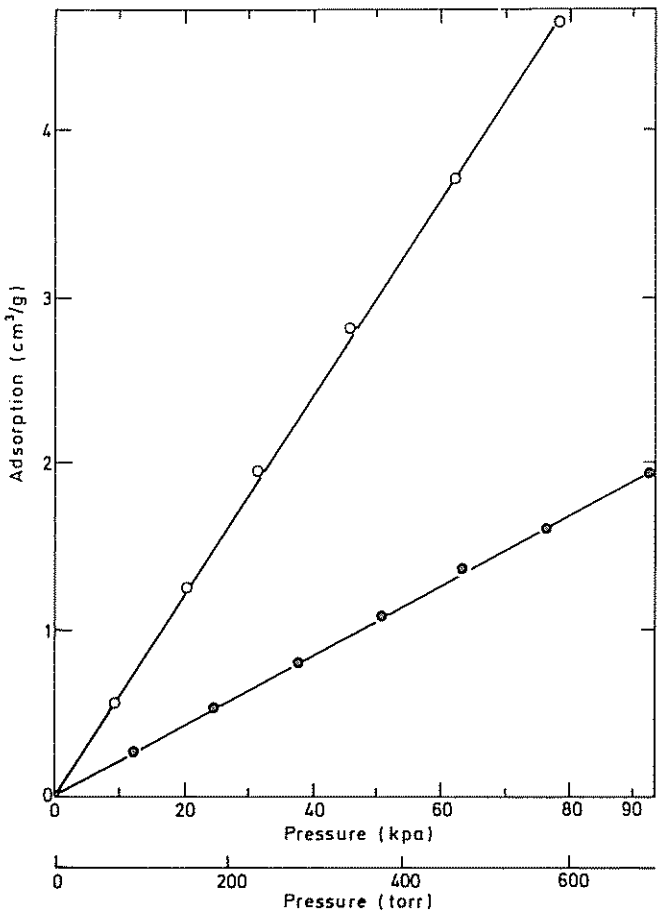


Figure 4 Isotherms for adsorption of oxygen (●) and nitrogen (○) at 25°C on 4A zeolite

produced at lower temperatures, a fraction of the oxygen is more tightly held. The phenol–formaldehyde carbon also shows somewhat higher oxygen adsorption. Furfuryl alcohol carbons do not show any preference for oxygen. The MSC-V and CXC carbons have the same capacity for both oxygen and nitrogen. Results with CXC may be indicative of the behaviour of all highly activated commercial carbons. The vinylidene chloride carbon, Saran carbon, and Carbosieve-B show somewhat higher nitrogen adsorptions compared with that of oxygen. It is interesting that these three carbons have vinylidene chloride as their main organic precursor. For Carbosieve-B, nitrogen also has a higher retention time in a chromatographic column[10] compared with that of oxygen.

Isotherms for the 4A zeolite are shown in *Figure 4*. The sequence of isotherm determination was oxygen first on the degassed sample, followed by nitrogen after 30 min degassing at adsorption temperature. Both gases could be removed completely by degassing. Adsorption of nitrogen is 2·76 times as high as oxygen adsorption. These adsorption data cannot be explained in terms of molecular sieving because nitrogen is a larger molecule. The different factors causing specificity in physical adsorption have been discussed by Barrer[11]. Nitrogen possesses a permanent quadrupole moment. The local electrostatic field of the ionic zeolite surface has an associated field gradient which can interact strongly with the permanent quadrupole moment of nitrogen. For the zeolite–nitrogen system, Barrer's calculations show that the contribution of electrostatic energy (force-field gradient–quadrupole interaction) to the heat of adsorption is significant; and this is the reason for the selectivity shown by zeolites towards nitrogen as compared with oxygen or argon. Zeolites, therefore, can also be used for partial separation of oxygen and nitrogen from air. A separate paper, being prepared, will consider this possibility in some detail.

Adsorption data on the second group of samples. Adsorption data for nitrogen and oxygen at 79·8 kPa and 25°C for selected carbon samples are presented in *Table 4*. Surface areas of the samples in carbon dioxide and nitrogen are also given. The effect of heat-treatment temperature on the adsorption of oxygen and nitrogen is clearly shown for lignite sample PSOC-91. For the 700 and 800°C chars, values of O_2(I) are higher compared with that of nitrogen but values of second cycle adsorption, O_2(II), are lower than O_2(I). This clearly shows that part of the oxygen adsorbed is held strongly on the surface. There is no evidence of strongly held oxygen on the 900 and 950°C chars from PSOC-91. That is, O_2(I) and O_2(II) adsorption values are essentially equal. O_2(II) for the 950°C char is also larger than N_2 adsorption. The 800°C heat-treated chars from PSOC-190 and 181 also show irreversible oxygen adsorption, although the amounts of oxygen strongly held are not as high as is the case for the 800°C lignite char. The 900°C chars from PSOC-190 and 181 show selective oxygen adsorption. In going to 1000°C the capacity of these samples decreases, but the selectivity (the ratio of adsorption of oxygen to that of nitrogen) increases.

Adsorption isotherms for the 800°C char from PSOC-212 (−150 mesh) are shown in *Figure 5*. This sample has desirable properties, that is it has selectivity as well as reversible oxygen adsorption. It is noted that the slope of the oxygen isotherms is greater than that of the nitrogen isotherm, indicating that oxygen adsorption will be increasingly favoured with increasing pressure. This char sample had the highest ratio for O_2/N_2 adsorption (at a particular adsorption pressure) among all the coal-char samples produced. Comparing results on the −150 mesh fraction of PSOC-212 with the 20 X 40 mesh fraction shows the importance of another variable. That is, both the capacity and selectivity for oxygen is lower on the 20 X 40 mesh material. The optimum heat-treatment temperature for PSOC-212 is about 800°C, as the 900°C char shows poorer adsorption capacity and selectivity.

Adsorption results for the coal samples considered so far show that: (1) the rank of the parent coal determines the pore structure developed in the char and (2) the optimum temperature for the development of selective adsorption properties is also a function of rank. Sorption data on the carbons obtained from PSOC-135 by a two-step process of preoxidation and subsequent heat treatment show that selective oxygen adsorbents can also be obtained from medium-volatile caking coals. For this preparative procedure two other variables, temperature of preoxidation and extent of preoxidation, are introduced in addition to the final heat-treatment temperature. When the final heat-treatment temperature is held at 900°C, it is seen from *Table 4* that about 200°C is the optimum preoxidation temperature. Samples preoxidized at 250°C show no selectivity.

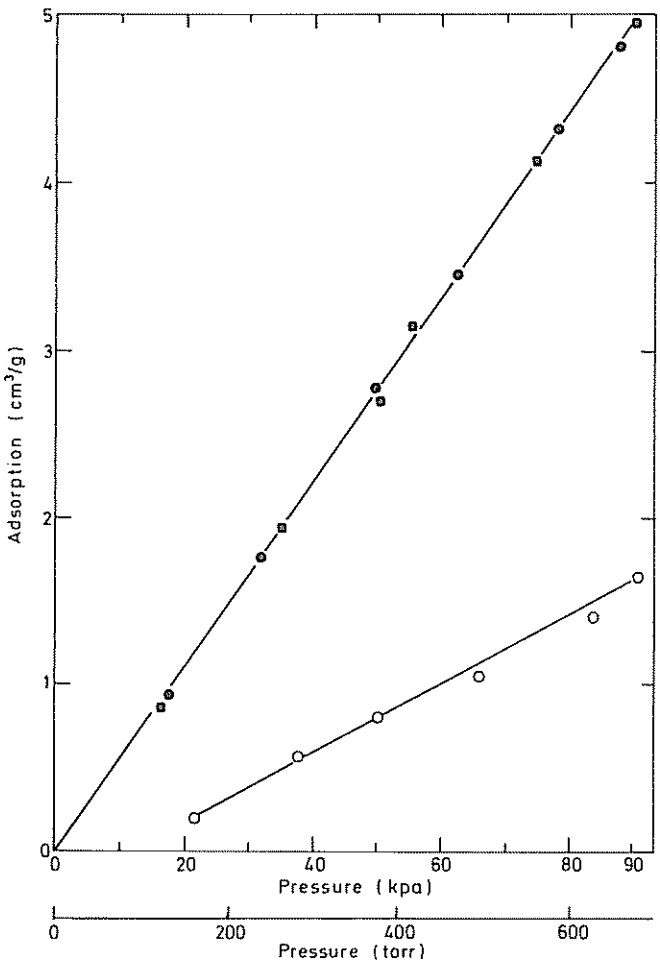
Adsorption results on the two coconut chars show that they are selective adsorbents for oxygen. The capacity of the char prepared at 950°C is lower than that prepared at 800°C, but its selectivity is better.

Rate of adsorption of oxygen and nitrogen on selected samples

Results presented so far show that significant nitrogen

Table 4 Adsorption of oxygen and nitrogen by different carbons

Sample No.	Sample description	Sieve size (Tyler)	Preoxidation Temp (°C)	Preoxidation Time (h)	Heat-treatment temp. (°C)	Surface area (m^2/g) CO_2	Surface area (m^2/g) N_2	Adsorption at 25°C and 79·8 kPa (cm^3/g) N_2	O_2(I)	O_2(II)
7	PSOC-91	40 X 70	None		700	616	43	5·5	8·4	6·0
18	PSOC-91	40 X 70	None		800	659	6·9	5·9	8·5	6·1
19	PSOC-91	40 X 70	None		900	662	9·1	6·2	6·3	6·1
20	PSOC-91	40 X 70	None		950	559	5·2	4·2	5·1	5·2
21	PSOC-138	40 X 70	None		1000	528	13	4·8	4·2	4·1
22	PSOC-190	40 X 70	None		800	938	24	3·2	4·6	3·5
23	PSOC-190	40 X 70	None		900	559	5·2	1·3	2·8	2·6
24	PSOC-190	40 X 70	None		1000	223	6·9	0·3	0·7	0·8
25	PSOC-181	40 X 70	None		800	627	89	4·1	5·4	4·8
26	PSOC-181	40 X 70	None		900	705	12	2·9	4·8	4·6
27	PSOC-181	40 X 70	None		1000	287	5·1	0·9	2·0	1·9
28	PSOC-212	20 X 40	None		800	650	<1·0	0·9	2·6	2·6
29	PSOC-212	−150	None		800	714	<1·0	1·3	4·4	4·4
30	PSOC-212	−150	None		900	425	<1·0	0·5	0·8	0·8
31	PSOC-212	−150	165	48	800	750	104	5·9	6·1	6·2
32	PSOC-135	40 X 70	150	125	900	220	1·4	0·5	1·6	1·6
33	PSOC-135	40 X 70	210	72	900	481	11·0	1·3	2·6	2·5
34	PSOC-135	40 X 70	210	144	900	763	7·6	1·9	3·7	3·6
35	PSOC-135	40 X 70	250	120	900	404	48	5·0	5·4	5·4
36	PSOC-135	40 X 70	250	210	900	680	104	5·1	5·4	5·4
37	Coconut shell	20 X 40	None		800	1168	<1·0	2·1	5·3	5·3
38	Coconut shell	20 X 40	None		950	800	<1·0	1·0	3·5	3·6



gure 5 Isotherms for adsorption of oxygen(I) (●), oxygen(II) (■), and nitrogen (○) at 25°C on sample 29 produced from coal PSOC-212

Table 5 Rates of oxygen and nitrogen adsorption

Sample No.	Adsorption at 24 h (m^3/g) O_2	Adsorption at 24 h (m^3/g) N_2	Initial slope ($min^{-1/2}$) O_2	Initial slope ($min^{-1/2}$) N_2	$(D_{O_2}/D_{N_2})_{initial}$
28	2·37	2·13	0·241	0·110	2·19
29	2·39	2·18	0·178	0·059	3·01
37	2··'3	2·50	0·213	0·059	3·60
38	2·59	2·14	0·123	0·033	3·73

adsorption takes place for all the carbon samples, that is the best carbons are not true molecular sieves. Higher oxygen uptake may largely be due to a higher rate of adsorption and not due to inherent differences in adsorptivities at equilibrium. To investigate the phenomenon further, rates of adsorption of oxygen and nitrogen were measured for four samples at 25°C and a constant pressure of 26·6 kPa. A time of 24 h was allowed for equilibrium. Rate data are presented in *Table 5*. The fractional approach to equilibrium V_t/V_∞ (where V_t = adsorption at time t and V_∞ = adsorption at 24 h) was plotted against $t^{0.5}$ (t = adsorption time). The slope of such a plot at small values of t (initial slope) is proportional to the diffusion coefficient of the particular gas into the pore structure of the carbon[12]. The ratio of the initial slopes of oxygen and nitrogen is, therefore, equal to the ratio of the initial diffusion coefficients of the two gases.

Comparing the equilibrium adsorption of the two gases, even though the adsorption of oxygen is higher for each sample, a major fraction of the pore area is available to nitrogen. The initial rate of adsorption, however, is significantly higher for oxygen. For a separation process using

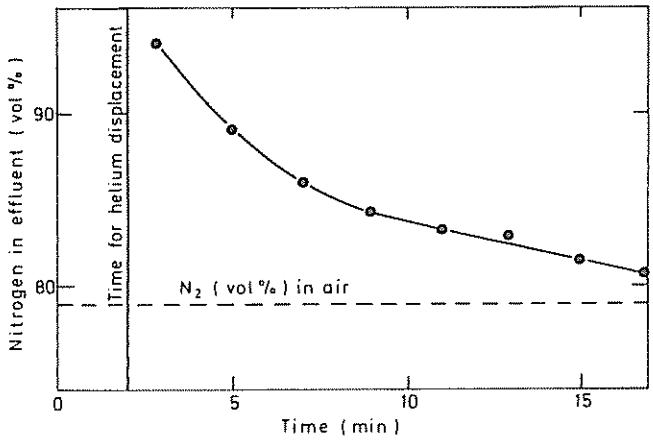


Figure 6 Variation in concentration of nitrogen in effluent with time of passage of air through bed of coconut char sample 38 at 0°C

Table 6 Concentration of oxygen over different carbonaceous solids

Sample No.	Volume of desorbed gas (cm^3/g)	Oxygen content (vol.%)
1	4·98	26·2
20	7·02	27·5
21	6·42	26·1
28	3·48	36·8
29	4·68	37·6
30	2·55	24·0
37	3·66	45·5
38	2·04	45·8

these carbons advantage has to be taken of this rate difference. Short adsorption times will preferentially favour oxygen uptake. On the other hand, utilization of the potential adsorption space will not be favoured by short adsorption times. The optimum adsorption time, therefore, has to be experimentally determined for a particular carbon at given values of the other process variables like temperature and pressure.

Again, results in *Table 5* show the importance of particle size on selectivity behaviour. Equilibrium adsorption values of nitrogen and oxygen are the same for both the 20 X 40 and −150 mesh samples of PSOC-212, but the ratio of initial rates of oxygen and nitrogen uptake are significantly different. The sample of smaller particle size has the higher ratio.

The coconut-char samples have a high value for the ratio of initial rates, when using the 20 X 40 mesh fraction. Results for other particle sizes were not determined.

Selective concentration of oxygen

Desorbed gas from atmospheric-pressure adsorption. As described in the Experimental Section, air was passed through a bed of carbon and the effluent gas analysed at intervals of 2 min. A typical curve showing the nitrogen content in the effluent with time of air flow is shown in *Figure 6*. The sample used was coconut char sample No.38. The air flow rate was 15 cm^3/min and the adsorption temperature 0°C. With this flow rate the time required to displace the helium in the tube is estimated to be 2 min. The curve shows that between 3 to 5 min the nitrogen concentration in the effluent averaged about 91·5%; that is, an effluent stream richer in nitrogen than is air can be obtained in a flow system using this carbon. The main interest of this work, however, was the concentration of oxygen; and so data on the 'desorbed gas' from different carbons are presented.

Carbons produced by heat treatment. Results of the desorption study for a number of samples are given in *Table 6*. The extent of oxygen enrichment shown by the two lignite chars (Samples 20 and 21) is not high, but the volume of desorbed gas is higher compared with the other samples. The phenol–formaldehyde char (Sample 1) behaves similarly to the lignite chars. For these samples the adsorption values of pure oxygen and nitrogen (shown in *Tables 3* and *4*) are not very different. For coal PSOC-212 (Samples 28–30), the performance of the 900°C char is poor compared to that of the 800°C char. These results also show that the adsorption of pure components (*Table 4*) can be used as a good indicator of the degree of selectivity to be expected from mixtures of oxygen and nitrogen. Using a 20 X 40 mesh particle size of PSOC-212 instead of −150 mesh material resulted in little change in oxygen content of the desorbed gas but a significant decrease in total amount of gas desorbed. The coconut chars show the largest concentration of oxygen, the 800°C sample also releasing a reasonable total volume of gas on desorption.

Carbons obtained by preoxidation followed by heat treatment. Coal samples PSOC-127, 135, and 212 were preoxidized prior to producing a char. PSOC-127 and 135 are coking coals and the cokes obtained from them by direct carbonization above 800°C have very low areas. PSOC-212, on the other hand, produces a char showing selective oxygen adsorption. This sample was preoxidized to find out whether the adsorption capacity of the char could be increased without decreasing significantly its selectivity.

For coal PSOC-127 three samples differing in extent of oxidation were produced, as seen in *Table 7*. It was found that on air oxidation at 200°C there was first an overall increase in weight of the sample. A maximum weight increase of 4·7% was found after 120 h of oxidation. On further oxidation, the weight started to decrease. Sample PSOC-135 showed similar oxidation characteristics to that of PSOC-127. For sample PSOC-212, the weight started to decrease after 2 h oxidation at 200°C. For this sample a lower oxidation temperature (165°C) was also used.

Results in *Table 7* show that the optimum preoxidation temperature for PSOC-127 is about 240°C. Sample No.41 shows about the same oxygen enrichment and capacity as shown by Sample No.29 in *Table 6*. This shows that a similar carbon can be produced from coking coal by a two-step process as produced from a non-coking coal by simple carbonization.

Comparing Samples 41 and 42 in *Table 7*, it is seen that the maximum heat-treatment temperature is a critical variable. An increase of 50°C in temperature results in almost complete loss of selectivity for the Sample 42.

For coal PSOC-135 the best preparation conditions have apparently not been achieved. Data on adsorption of pure gases (*Table 4*) by preoxidized and carbonized PSOC-135 suggest that the optimum preoxidation temperature for this coal would be lower than 250°C.

Results for Sample 31, compared with those of Sample 29 in *Table 6*, show that by preoxidation capacity can be

Table 7 Concentration of oxygen over different carbonaceous solids (results from atmospheric pressure sorption apparatus)

Sample No.	Coal	Particle size (Tyler mesh)	Air-oxidation conditions			Heat-treatment temp. (°C)	Volume of de-sorbed gas (cm^3/g)	O_2 content (vol.%)
			Temp. (°C)	Time (h)	Weight change (%)			
31	PSOC-212	−150	165	12	−6·5	800	10·6	21·5
32	PSOC-135	40 X 70	150	150	+5·2	900	1·68	27·8
33	PSOC-135	40 X 70	210	130	0·0	900	2·31	28·4
34	PSOC-135	40 X 70	210	144	−1·1	900	3·69	31·5
35	PSOC-135	40 X 70	250	100	−8·1	900	7·62	27·3
39	PSOC-127	40 X 70	200	200	0·0	900	1·53	32·3
40	PSOC-127	40 X 70	210	170	−1·0	900	1·56	32·8
41	PSOC-127	40 X 70	240	120	−10·7	900	4·35	37·5
42	PSOC-127	40 X 70	240	120	−10·7	950	1·14	21·5
43	PSOC-212	−150	165	12	−6·5	900	10·1	25·5
44	PSOC-212	−150	165	12	−6·5	950	5·76	37·8
45	PSOC-212	−150	200	6	−21·0	900	7·67	31·3
46	PSOC-212	−150	200	6	−21·0	950	6·25	31·6

Table 8 Concentration of oxygen over Sample No.29 in pressure adsorption apparatus

Run No.	Inflowing gas (% O_2)	Temp. of adsorption (°C)	Final adsorption pressure (MPa)	Time allowed (min)	Residual pressure (kPa)	O_2-rich gas		Yield
						Volume (cm^3/g)	O_2 (%)	
1	21·0	25·0	2·10 (305 psi)	2·0	227	6·1	36·0	0·12
2	21·0	25·0	2·92	2·0	227	7·3	40·1	0·11
3	21·0	25·0	4·21	2·0	241	8·7	43·6	0·09
4	21·0	25·0	5·90	2·0	241	9·9	47·6	0·07
5	21·0	25·0	5·96	5·0	585	23·0	38·2	0·16
6	21·0	25·0	5·94	5·0	725	26·4	35·6	0·18
7	21·0	0·0	2·07	5·0	227	7·1	38·1	0·14
8	21·0	0·0	2·87	5·0	227	8·3	42·5	0·12
9	21·0	0·0	4·10	5·0	255	10·9	45·5	0·11
10	21·0	0·0	5·71	5·0	241	12·4	49·6	0·09
11	35·0	25·0	2·10	2·0	207	9·9	55·9	0·19
12	35·0	25·0	2·92	2·0	207	10·8	58·9	0·15
13	35·0	25·0	4·17	2·0	241	13·3	60·3	0·14
14	35·0	25·0	5·79	2·0	255	14·8	64·2	0·12
15	35·0	0·0	2·08	5·0	227	8·9	58·7	0·18
16	35·0	0·0	2·80	5·0	207	10·4	63·0	0·15
17	35·0	0·0	3·96	5·0	234	13·1	66·6	0·14
18	35·0	0·0	6·29 (913 psi)	5·0	241	15·6	68·3	0·12

increased but at the cost of selectivity. Data for Samples 43 and 44 show that selectivity can be restored by increasing heat-treatment temperature; but as discussed previously, capacity falls if heat-treatment temperature is too high.

Oxygen-rich gas from batch-type operation at higher pressures. Seven samples were selected for testing in a batch-type operation at higher pressures. Runs were made at 25°C and 0°C in the starting pressure range 2·2 to 6·4 MPa. Different times of adsorption were allowed in the range 0·5 to 7 min. As feed, both air and a mixture of 35% O_2–65% N_2 were used. Carbon samples were allowed a fixed time of adsorption at elevated pressure, after which the pressure was quickly (0·50 min) reduced to a lower 'residual pressure'. The amount of gas collected in going from the 'residual pressure' to 13·79 kPa (2 psi) was termed 'oxygen-rich gas'. The amount of 'oxygen-rich gas' per gram of sample, its oxygen content, and the ratio of the volume of oxygen-rich gas to the volume of gas originally charged (yield) are shown in *Table 8*. For brevity, only results for Sample 29 are included.

The effect of pressure during adsorption on the volume of oxygen-rich gas and its content, when air is the inflowing gas, is shown graphically in *Figure 7* for two adsorption temperatures. The time allowed for adsorption at 25°C was 2 min whereas the time allowed at 0°C was 5 min. The residual pressure in all the runs was essentially the same (245 kPa). It is seen that by keeping the adsorption and residual pressure constant, both the volume of rich gas and its oxygen content increases with increasing pressure. This is true for all the samples studied. Enrichment of oxygen

is favoured at lower temperature but longer adsorption time is required to obtain a comparable volume of rich gas because diffusion into the micropores is slower. Considering the cost of cooling the adsorption column as well as the need for greater cycling time, operations at ambient temperature may be favoured.

It is seen from *Table 8* that the yield of rich gas decreases with increasing adsorption pressure. For example, the yield decreases from 0·12 to 0·07 in going from 2·14 to 6·99 MPa for the runs with air at 25°C. Increasing residual pressure produces an increase in the volume of rich gas but a decrease in its oxygen content. This is seen by comparing runs 5 and 6 in *Table 8*. Increasing adsorption time increases the volume of oxygen-rich gas and at the same time decreases its oxygen content, as was seen from runs on Sample 44. Comparing the performance of Samples 28 and 29, Sample 29 produced higher oxygen enrichment, which is in agreement with its higher ratio of initial rate of oxygen to nitrogen uptake (*Table 5*).

Results obtained with the 35% O_2–65% N_2 mixture parallel those obtained with air as the feed gas. Not only is the oxygen content of the product gas increased but also the yield of gas rises dramatically.

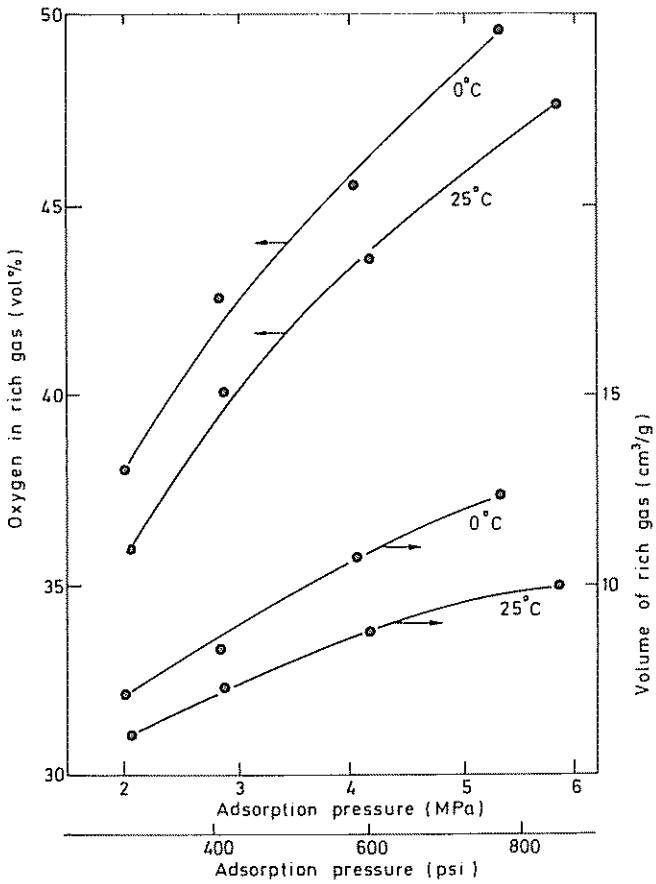


Figure 7 Volume and oxygen content of gas recovered following exposure of sample 29 to air at different pressures and temperatures. Desorption conducted at adsorption temperature

Operation with carbon beds in series

In this study the maximum concentration of oxygen produced in the rich gas was about 47%, with air as the inflowing gas at 25°C. A higher oxygen content can only be reached if the rich gas from the first column of carbon is used as feed to a second column. Operations with three carbon columns have been simulated by using air, 35% O_2–65% N_2, and 59% O_2–41% N_2 as feed gases for Samples 29 and 37. Results are shown in *Table 9*. It is seen that by using three columns a stream of about 80% O_2 can be produced. The yield of rich gas at each stage is slightly higher for the coconut char than for the char from PSOC-212. The yield depends, to a large extent, on the free volume of the adsorption column. In an idealized column where the volume of the connecting tubes as well as the free space above the bed are made small compared with the volume occupied by the carbon, the yield of rich gas will be higher than the figures shown in *Table 9*. Calculations of an upper level of theoretical yield can be made for Sample 29, assuming that no gas was removed from the pore volume of the char during the time of rapid reduction of adsorption pressure to residual pressure. Sample 29 had values of mercury and helium densities of 1·1 and 1·8 g/cm^3 respectively, giving an open-pore volume of 0·355 cm^3/g. The sample packed to a specific volume of 1·36 cm^3/g, the solid occupying 0·91 cm^3/g of this volume. This leaves a volume between particles of 0·45 cm^3/g. The volume of the column used was about 48 cm^3. The 15 g sample used would occupy 20·4 cm^3, leaving a free space above the sample of 27·6 cm^3. For the run having a final adsorption pressure of 5·02 MPa and a residual pressure of 735 kPa, a theoretical yield of 24·0% is calculated. This is compared with the experimental yield of 18%, indicating as expected that some gas was removed from the pore volume of the carbon during pressure reduction from 5·02 MPa to 735 kPa. At least one reason why the yield from Sample 37 is higher than that from Sample 29 is the larger particle size

Table 9 Concentration of oxygen over different carbons at 25°C in pressure adsorption apparatus

Inflowing gas (% O_2)	Final adsorption pressure (MPa)	Time allowed (min)	Residual pressure (kPa)	O_2-rich gas		Yield
				Volume (cm^3)	O_2 (%)	
			SAMPLE 29			
21	5·95 (860 psi)	5	725	26·5	35·6	0·18
35	6·05	5	415	24·2	58·9	0·16
59	6·1	2	275	22·1	82·7	0·14
			SAMPLE 37			
21	5·8	7	790	32·0	35·2	0·23
35	5·9	5	380	27·7	58·9	0·20
59	5·95	2	240	24·7	81·2	0·18

of Sample 37; a smaller fraction of gas within the pore volume of the particles is removed as a result of pressure reduction. If the free space above the bed were removed completely, the theoretical yield would be increased from 24·0 to 51% for the run discussed above.

UMMARY

Results of this investigation indicate that it is possible to produce carbons from HVC or subbituminous coals by simple heat treatment in the temperature range 800 to 900°C that will selectively adsorb oxygen preferentially to nitrogen from air. Similar carbons can be obtained from higher-rank caking coals by a two-step process of initial low-temperature oxidation followed by heat treatment. The adsorbed gas can be desorbed reversibly at adsorption temperatures of 0°C or 25°C, the percentage of oxygen in the product gas increasing with adsorption pressure. Enrichment is also favoured at the lower adsorption temperature. Working with three beds of carbon in series, a gas containing 80% oxygen can be obtained from air.

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