

Characteristics of chars produced from lignites by pyrolysis at 808°C following rapid heating

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Closely size graded lignite particles were pyrolysed at 808°C in a laminar flow furnace for times up to 1 s following heating up at 8×10^3 °C/s. Following pyrolysis, the chars were rapidly cooled — at about 3×10^4 °C/s. Weight losses were measured as a function of pyrolysis time. The following measurements were made on the chars: (1) nitrogen and carbon dioxide specific surface areas, using adsorption data at 77 and 298 K, respectively; (2) apparent and true densities obtained from mercury and helium displacements; (3) total open-pore volumes and porosities; and (4) particle size distributions. Results show, with increasing pyrolysis time, that: (i) specific surface areas increase, (ii) helium densities increase, (iii) mercury densities decrease, (iv) open-pore volumes increase, and (v) weight-mean particle size decreases. Chars produced following rapid heating have higher open-pore volumes than those produced following slow heating.

Volatile matter release during pyrolysis of coal brings about a development of internal porosity. This results directly from one or more of the following: (1) opening of previously closed pores; (2) creation of new pores; and (3) enlargement of preexisting and/or newly developed pores. The development of porosity gives rise to changes in pore structural parameters such as densities, specific surface areas, pore-size distributions, total open-pore volumes and porosities, and average pore diameter. Development of internal porosity can be followed by measuring changes in the physical structural parameters given above. This type of information is important because the nature of the pore structure in a particular coal and char produced therefrom determines to a large degree the level of its reactivity during gasification or combustion. Accordingly, this study was aimed at following changes in the internal pore structure of coal during its pyrolysis following rapid heating. Selected structural parameters, namely nitrogen and carbon dioxide specific surface areas, and mercury and helium densities, were correlated with weight loss to observe the direct effect of this last parameter on the pore structure during the pyrolysis process.

EXPERIMENTAL

Pyrolysis

Rapid heating. The method used to produce the chars was that of Badzioch and Hawksley¹. The equipment is described in detail elsewhere^{2,3}. The essence of the equipment is a vertical tube furnace, heated electrically, carrying a stream of down-flowing preheated nitrogen into which finely ground coal is continuously mixed. The ground coal is injected at the top of the furnace on the tube axis and carried in a stream of cold nitrogen. Design requires that the mass flow of cold nitrogen plus coal is small compared with the heated nitrogen (ratio 1 to 13) so that the cooling

effect from this addition is also small. Plunging the particles into hot gas also results in rapid heating, estimated in these experiments at 8×10^3 °C/s². Proper design of the injector reduces radial spread of the particle stream and to a degree keeps the particles off the furnace wall. This is assisted by maintaining laminar flow with velocities high enough (102 cm/s and $Re = 440$) for gas/particle velocities to be neglected but otherwise as low as possible to give significant retention times. The particles are captured and quenched in an adjustable water-cooled sampling tube. The cooling rate was estimated to be 2.7×10^4 °C/s². Residence time is varied by moving the sampling tube up and down. Maximum residence time was 300 ms, but this was extended to 1 s by recycling, as described in more detail below.

The (main) pyrolysis furnace consisted of a mullite tube 58 cm long, 5.1 cm i.d., and 5.7 cm o.d. The electric windings were held on an outer concentric mullite tube 51 cm long, 6.4 cm i.d., and 7.0 cm o.d. This was wound with two different sizes of Kanthal A-1 resistance wire for a length of 46 cm at 1.5 windings/cm. This winding was provided with six shunt taps to permit adjustment of the temperature profile of the gas in the tube. By appropriate adjustment of the shunts, uniform axial gas temperatures (± 5 °C) were obtained over a length of 23 cm, as measured by a suction pyrometer.

Pyrolysis was conducted at a gas temperature of 808°C. Flow rates were as follows: (1) coal feed, about 0.5 g/min, (2) main nitrogen stream, 30 000 cm³ (STP)/min, (3) carrier nitrogen stream, 2000 cm³/min, and (4) collector probe suction rate, 14 000 cm³/min. About 8 g of char were needed for subsequent proximate analyses and for gas adsorption and density measurements. Maximum run time to obtain the necessary samples was up to 3 h per station in the pyrolysis tube.

Slow heating. About 50 g of a size-graded coal sample

was placed into a small fluid-bed reactor (a quartz tube of 5.08 cm inner diameter and about 90 cm in length), and nitrogen was passed into the bed until full fluidization of particles occurred. The system was flushed for about 30 min. Then the sample was heat-treated at a rate of $\approx 10^\circ\text{C}/\text{min}$ to a final temperature of 808°C . The temperature rise was monitored by a sheathed thermocouple placed into the coal bed. As soon as 808°C was reached, the reactor was pulled out of the furnace and allowed to cool while continuing to pass nitrogen through the bed.

Char characterization

Mercury and helium displacements. Char densities were measured by mercury and helium displacements, using apparatus and approaches described by Gan⁴ and Gan *et al.*⁵. Prior to measurement, samples were outgassed overnight at 115°C to a vacuum of 1 mPa or better.

Gas adsorption. Adsorption of nitrogen and carbon dioxide were conducted on selected samples at 77 and 298 K, respectively. The equipment and experimental method used have been described by Gan⁴ and Gan *et al.*⁵. Samples were outgassed overnight at 115°C to a vacuum of 1 mPa or better prior to adsorption runs. Adsorption time allowed for each adsorption point was 45 min. The Brunauer–Emmett–Teller (BET)⁶ and Dubinin–Polanyi⁷ equations were used to calculate surface areas from nitrogen and carbon dioxide adsorption.

Coals studied

Pyrolysis of Montana and North Dakota lignites was studied. Table 1 presents analyses of these coals.

RESULTS

Weight loss on pyrolysis

General behaviour. Loss in weight of the coal flowing through the furnace was determined as a function of time. Figure 1 presents results for three particle sizes of lignite PSOC-90. Time was initially measured from the point of entry into the furnace and calculated by assuming uniform velocity at constant temperature (808°C) for the bulk of the flow (although 1/13th by weight was being heated up). Weight loss was found to start at a false origin (as also found by Badzioch and Hawksley¹) 95 ms after entry. In Figure 1

this heating period has been subtracted out. Weight loss was determined using ash as a tracer in the conventional manner; this involved measuring the ratio of combustible to ash in the char samples obtained by ashing.

Estimates of heating rates of particles plunged into hot gas indicate that even at $8000^\circ\text{C}/\text{s}$ heating rate no significant temperature gradient exists in the particles on reaching reactor temperature (808°C) after 95 ms^2 .

The variation in weight loss between successive determinations was examined on one size grade (270 x 400 U. S. mesh) of PSOC-246 in the following manner. Three repeat measurements were made at each of seven positions in the furnace reaction zone. The standard deviation from all these samples was subsequently used to determine a confidence limit on the means of weight loss. For weight loss, the 95% confidence limit was found to be $\pm 0.79\%$.

Effects of heat-up time or recycle. Samples of chars from PSOC-246 were recycled through the furnace one or more times with two objectives in view: to examine the possible influence of the heating-up time on weight loss and to determine the feasibility of extending pyrolysis time by recycling. To test the effects of recycle, the weight loss obtained in a given once-through transit time was compared with the weight loss for the same isothermal and cumulative transit

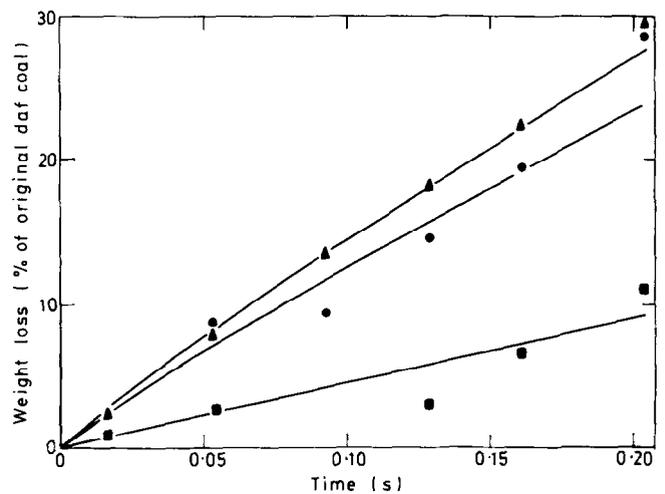


Figure 1 Variation of weight loss with isothermal pyrolysis time for various original sieve sizes of PSOC-90: \blacktriangle 200 x 270; \bullet 140 x 200; \blacksquare 70 x 100

Table 1 Analysis of coals

Coal identification			Analysis					
Code No.	Source area	ASTM rank	Proximate analysis (wt %):	(dry)	(daf)	Ultimate analysis (wt %)	(dry)	(daf)
PSOC-90	Lower Seam, Savage Mine, Montana	Lignite	Volatile matter	39.9	43.5	C	64.8	71.6
			Fixed carbon	51.7	56.5	H	4.4	4.9
			Ash	8.4	—	N	0.7	0.8
						S	0.3	0.3
						O	20.3	22.4
			Ash			9.5	—	
PSOC-246	Coteau Seam, Glen Harold Mine, North Dakota	Lignite	Volatile matter	43.7	47.5	C	64.1	71.0
			Fixed carbon	48.3	52.5	H	4.4	4.9
			Ash	8.0	—	N	1.4	1.6
						S	0.6	0.6
						O	19.8	21.9
			Ash			9.7	—	

Table 2 Effect of recycling on weight loss for different particle sizes of PSOC-246 coal

Recycle condition	Isothermal time (ms)	Total time (ms)	Weight loss (% of original dry-ash-free coal)			
			200 x 270	140 x 200	100 x 140	70 x 100
Once	110	300	10.1	11.4	—	3.7
Once	205	395	30.5	19.0	18.1	12.7
None	205	300	31.6	25.2	18.5	13.0

times involving one recycle. Typical results are summarized in Table 2, for four different sieve fractions (U.S. mesh) of PSOC-246. A once-through isothermal transit time of 205 ms could be accommodated, involving a preheating period of 95 ms for a total transit time of 300 ms.

Table 2 summarizes the following conditions for comparison. Line 1 gives weight loss of a sample that was removed after 55 ms of isothermal exposure and then recycled under the same conditions. Isothermal exposure was therefore 110 ms, with 190 ms of heating-up time for a total cumulative residence time of 300 ms. Line 2 gives weight loss for a sample recycled once for the same (190 ms) heating-up duration, but the isothermal exposure time was increased to 205 ms, for a total exposure time of 395 ms. Line 3 is for the once-through sample at 95 ms heating-up time and 205 ms isothermal exposure for a total exposure time of 300 ms. The conclusion is self-evident: weight losses were similar (with some question on the 140 x 200 mesh fraction) for equal isothermal exposure time; weight losses were clearly not similar at equal total exposure time. It is concluded, as have others previously¹, that there is no detectable or significant weight loss during periods of either very rapid heating or cooling. Even more significant, the pyrolysis mechanism is evidently unaffected at 808°C by the reaction being interrupted, that is total pyrolysis time being achieved by recycling.

Effect of increased pyrolysis time. Advantage was taken of the conclusions of the recycling experiments to extend the isothermal reaction time to 1 s. Figure 2 is typical of the results obtained for PSOC-246. As can be seen, the extended reaction time brought out a significantly different trend in the weight-loss behaviour, with a marked break in the plots for all three particle sizes shown – and with the location of the break at a reaction time that is essentially independent of particle size. Such a break in a cumulative reaction curve is characteristic of two independent parallel reactions, hinting at decomposition of two independent components. A kinetic treatment of these results is considered elsewhere³.

Percentage weight losses for PSOC-246 following its pyrolysis in the fluid bed were 49.3% (200 x 270 mesh), 47.7% (140 x 200 mesh), 41.6% (100 x 140 mesh), and 43.8% (70 x 100 mesh).

Densities, total open-pore volumes and porosities

Values of densities by mercury and helium displacement can be used to calculate

$$V_T = 1/\rho_{Hg} - 1/\rho_{He} \quad (1)$$

and

$$\theta = 100(1 - \rho_{Hg}/\rho_{He}) \quad (2)$$

where V_T is the total open-pore volume down to a pore diameter of about 0.42 nm and θ is the percentage porosity

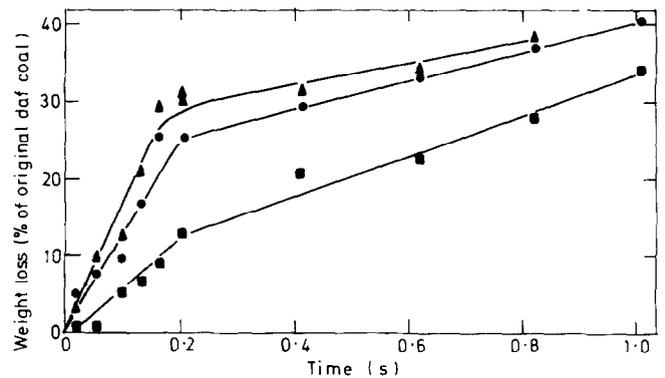


Figure 2 Variation of weight loss with isothermal pyrolysis time for various original sieve sizes of PSOC-246: \blacktriangle 200 x 270; \bullet 140 x 200; \blacksquare 70 x 100

within the particles. The measured densities were placed on an ash-free basis by taking 2.7 g/cm³ as the mercury and helium density of the ash⁸. The value taken for ash density, within limits, has a relatively small effect on the calculated values of V_T and θ .

Results are presented in Table 3 for one size grade of the Montana lignite and four size grades of the North Dakota lignite. They show the variation of these structural parameters (densities, total open-pore volumes and porosities) with particle size and pyrolysis time. At the 95% confidence level helium and mercury densities are known to within ± 0.01 g/cm³. However, no systematic statistical analysis has been made on the density values obtained from repeat runs.

In Figures 3 and 4 results for the change in densities with pyrolysis time for the 200 x 270 mesh fractions of PSOC-90 and PSOC-246 are shown. The helium density increased with short pyrolysis times and the mercury density decreased. Both densities reached essentially their limiting values for a pyrolysis time of 600 ms for PSOC-246. These changes in densities produced an increase in total pore volume and porosity, the values becoming essentially constant following a pyrolysis time of 600 ms.

The rate of change of densities with pyrolysis time is a function of initial coal particle size, as seen in Table 3. That is, the rate of change decreased as the lignite particle size was increased. This is seen, particularly, by comparing results for the 200 x 270 mesh and 70 x 100 mesh fractions of PSOC-246. It, therefore, took longer pyrolysis times for the chars to reach their limiting values of densities, total open-pore volume, and porosity as the particle size of the starting lignite was increased. Within experimental uncertainty, the limiting values were independent of particle.

Limiting densities following rapid heating of PSOC-246 to 808°C are in marked contrast to the values found for the chars produced following slow heating in the fluidized bed. Slow heating produces negligible differences in the mercury densities of the chars and original coals but much higher values of

Table 3 Densities, total open-pore volumes and porosities for lignites and chars

Coal	Original size grade (U.S. mesh)	Case ^a	ρ_{Hg} (g/cm ³)		ρ_{He} (g/cm ³)		V_T [cm ³ /g (daf)]	θ [% (daf)]
			(dry)	(daf)	(dry)	(daf)		
PSOC-90	(200 x 270)	ORO	1.31	1.25	1.51	1.45	0.110	13.7
		OR18	1.30	1.24	1.51	1.45	0.117	14.4
		OR55	1.31	1.25	1.54	1.48	0.124	15.5
		OR93	1.25	1.18	1.54	1.47	0.167	19.7
		OR130	1.19	1.12	1.56	1.49	0.222	24.8
		OR167	1.22	1.15	1.57	1.49	0.198	22.8
		OR205	1.18	1.10	1.62	1.54	0.259	28.5
PSOC-246	(200 x 270)	ORO	1.37	1.31	1.56	1.50	0.097	12.6
		OR205	1.04	0.96	1.76	1.68	0.446	42.8
		1R110	1.10	1.04	1.73	1.67	0.363	37.7
		1R205	0.98	0.91	1.77	1.69	0.507	46.1
		1R410	0.97	0.90	1.78	1.71	0.545	47.3
		2R615	1.00	0.92	1.82	1.75	0.516	47.4
		3R820	0.99	0.91	1.82	1.74	0.524	47.7
		FB	1.39	1.29	2.06	1.99	0.273	35.2
		PSOC-246	(140 x 200)	ORO	1.36	1.31	1.55	1.50
OR205	1.01			0.95	1.63	1.56	0.412	39.1
1R410	0.97			0.90	1.68	1.61	0.490	44.1
2R615	0.88			0.81	1.67	1.60	0.610	49.3
3R820	0.93			0.86	1.75	1.67	0.564	48.5
4R1025	0.98			0.89	1.82	1.74	0.549	48.8
FB	1.39			1.31	2.02	1.95	0.251	32.8
PSOC-246	(100 x 140)	ORO	1.36	1.31	1.57	1.52	0.105	13.8
		OR205	1.10	1.06	1.60	1.55	0.312	32.4
		1R410	0.93	0.87	1.65	1.58	0.517	44.9
		FB	1.42	1.34	2.07	2.01	0.249	33.3
PSOC-246	(70 x 100)	ORO	1.36	1.31	1.56	1.51	0.101	13.2
		OR205	1.22	1.17	1.59	1.54	0.198	23.3
		1R110	1.25	1.20	1.57	1.52	0.175	21.1
		1R410	1.10	1.04	1.62	1.56	0.321	33.3
		2R615	0.96	0.91	1.65	1.59	0.469	42.7
		3R820	0.92	0.86	1.72	1.66	0.560	48.2
		4R1025	0.96	0.90	1.76	1.70	0.523	47.0
		FB	1.43	1.34	1.99	1.92	0.225	30.2

^a These cases have the following explanation: R stands for recycle, the numeral in front of it stands for the number of recycles, and the number after it stands for the isothermal pyrolysis time (in milliseconds). Examples: (i) case ORO means zero recycle and zero pyrolysis time (this particular case is for the raw material); (ii) case 4R1025 means four recycles for a cumulative pyrolysis time of 1025 ms. FB identifies the fluid-bed chars.

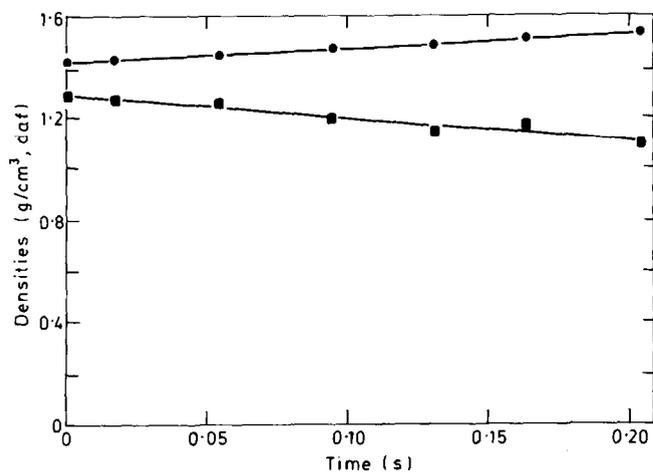


Figure 3 Variation of mercury (■) and helium (●) densities with isothermal pyrolysis times for 200 x 270 mesh PSOC-90

helium densities for the chars. As a result, the mercury and helium densities of the chars produced on slow heating are higher than the resulting values produced upon rapid heating.

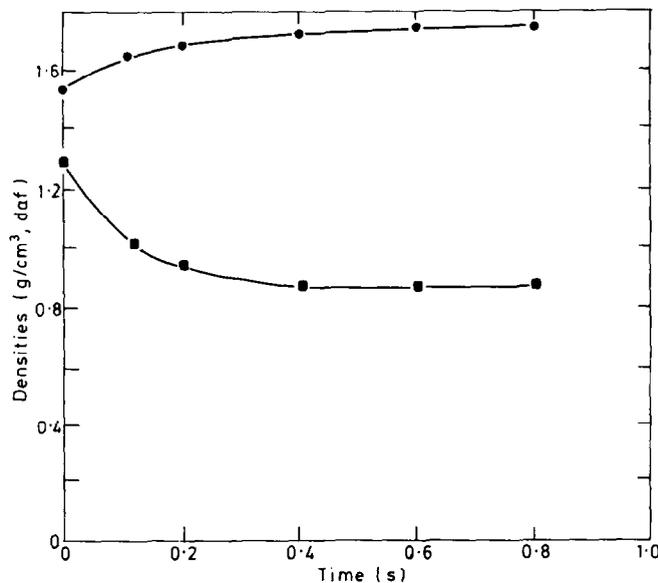


Figure 4 Variation of mercury (■) and helium (●) densities with isothermal pyrolysis times for 200 x 270 mesh PSOC-246

Pore volumes of chars produced upon slow heating were less than one-half the values for chars produced by rapid heating.

Specific surface areas

Results are presented in Table 4 for one size grade of the Montana lignite and four size grades of the North Dakota lignite. These data show the variation of nitrogen and carbon dioxide specific surface areas with particle size and pyrolysis time. The surface area of the ash is considered negligible when placing the results on an ash-free basis.

In Figures 5 and 6 results for the change in surface areas with pyrolysis time for the 200 × 270 mesh fractions of PSOC-246 are shown. Both surface areas increase with pyrolysis time. However, in contrast to densities, which change most sharply during the first 200 ms of pyrolysis for PSOC-246, surface areas change most sharply for pyrolysis times greater than 200 ms. As discussed later, surface areas which are reported depend significantly on outgassing temperatures used prior to adsorption measurement.

Particle-size distribution

Results from dry sieve analyses of the lignites and chars gave rectilinear plots on Rosin–Rammler graph paper, expressing the variation of weight % oversize (R) with particle size (x). Rosin–Rammler parameters (Table 5) are given by the relation⁹:

$$R = 100 \exp[-(x/k)^n] \quad (3)$$

where R and x are as defined before, k is a measure of the fineness of the materials and is equal to x when $R = 100/e = 36.79$, and n (the slope of the line) is a measure of size dispersion, a low value indicating a wide dispersion. It follows that $\bar{x} = [k] [\phi(n)]$ where \bar{x} is the weight mean particle size and $\phi(n)$ is the gamma function $\Gamma(1 + 1/n)$. Details of this calculation are given elsewhere².

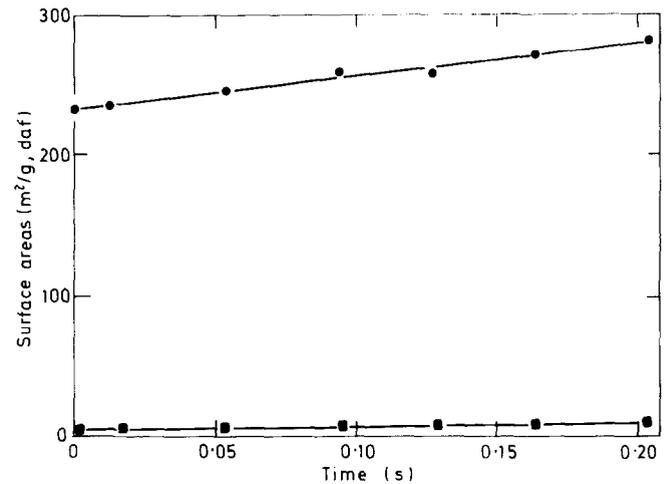


Figure 5 Variation of nitrogen (■) and carbon dioxide (●) specific areas with isothermal pyrolysis times for 200 × 270 mesh PSOC-90

Table 4 Specific surface areas for lignites and chars

Coal	Original size grade (U.S. mesh)	Case	N ₂ (m ² /g)		CO ₂ (m ² /g)	
			(dry)	(daf)	(dry)	(daf)
PSOC-90	(200 × 270)	ORO	1.1	1.2	218	238
		OR18	1.7	1.9	218	239
		OR55	1.7	1.9	224	247
		OR93	1.9	2.1	238	263
		OR130	1.2	1.3	231	253
		OR167	4.0	4.5	238	267
		OR205	4.3	4.9	245	276
PSOC-246	(200 × 270)	ORO	<1	<1	190	207
		OR205	3.5	3.9	194	213
		1R110	2.6	2.9	173	190
		1R205	3.5	3.9	197	222
		1R410	30.0	33.8	238	268
		2R615	84.0	95.0	286	324
		3R820	—	—	326	372
		FB	139	161	537	621
PSOC-246	(140 × 200)	ORO	<1	<1	184	199
		OR205	2.9	3.2	218	242
		1R410	3.9	4.3	218	243
		2R615	12.9	14.5	252	283
		3R870	16.3	18.4	269	304
		4R1025	32.2	36.6	340	386
		FB	162	184	483	548
PSOC-246	(100 × 140)	ORO	2.3	2.5	150	162
		OR205	4.3	4.6	163	179
		1R410	5.4	7.1	258	286
		FB	102	115	469	528
		PSOC-246	(70 × 100)	ORO	<1	<1
OR205	3.9	4.2		163	177	
1R110	2.2	2.4		187	201	
1R410	6.8	7.4		231	252	
2R615	5.7	6.2		245	268	
3R820	30.4	33.5		286	315	
4R1025	27.3	30.3		292	324	
FB	96	109	456	511		

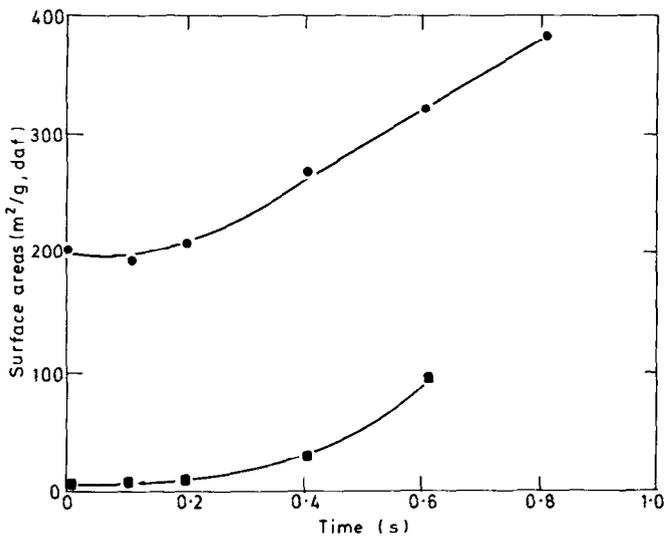


Figure 6 Variation of nitrogen (■) and carbon dioxide (●) specific areas with isothermal pyrolysis times for 200 x 270 mesh PSOC-246

Table 5 Rosin-Rammler parameters for PSOC-246 lignite and chars

Original size grade (U. S. mesh)	Case	<i>n</i>	<i>k</i> (μm)	<i>φ</i> (<i>n</i>)	\bar{x} (μm)
200 x 270	ORO	15.0	66	0.968	64
	OR205	6.6	63	0.933	59
	IR410	6.6	63	0.930	59
	FB	5.3	56	0.921	52
140 x 200	ORO	11.8	90	0.959	86
	OR205	5.0	88	0.918	81
	IR410	5.1	92	0.918	84
	FB	2.8	78	0.891	70
100 x 140	ORO	21.0	130	0.974	127
	OR205	8.0	130	0.942	122
	IR410	7.1	128	0.936	120
	FB	9.0	100	0.947	95
70 x 100	ORO	16.0	185	0.969	179
	OR 205	6.0	170	0.928	158
	IR410	7.6	170	0.941	160
	FB	11.0	150	0.955	143

From probability considerations it is found that¹⁰:

$$F(x) = 100nbx^{n-1}\exp(-bx^n) \quad (4)$$

where $F(x)$ is the probability of finding particles of size x , b is a characteristic constant [$b = (1/k)^{-n}$], and n and k are as defined before. Selected results are given in Figure 7. Note should be taken that equation (4) gives a skewed rather than a normal distribution.

Rosin-Rammler parameters for PSOC-246 feed coal and selected chars produced by both rapid and slow heating are given in Table 5. Pyrolysis, in every case, produces a broader distribution in particle size of the char than that in the starting lignite sieve fraction. Also, in every case, pyrolysis results in some decrease in the weight-mean particle size, the decrease being most marked when a slow heating rate is used.

DISCUSSION

Coals are composed of aromatic and hydroaromatic building blocks, containing more or less crosslinks between the building blocks and functional groups at their periphery. Upon the pyrolysis of coal, functional groups are removed as volatile matter, some crosslinks are broken, and hydroaromatic building blocks are converted to additional aromatic building blocks and then to small carbon crystallites. The latter process involves dehydrogenation and condensation reactions. Breakage of crosslinks permits improved alignment of the building blocks. Whether the char particles remaining have a more open or less open pore structure than that in the original coal depends upon a balance between additional pore volume created by volatile matter release and loss of pore volume caused by enhanced alignment and growth of the planar building blocks. The balance is a function of the rank of the starting coal^{11,12}, maximum heat-treatment temperature (HTT)^{11,12}, heating rate to maximum temperature, and residence time at maximum temperature.

Results presented in this study on weight loss of two lignites as a result of pyrolysis for short times at 808°C are helpful to our further understanding of the conversion of precursor coals to chars. First, it is clear that devolatilization and consequent weight loss are rapid, even at a pyrolysis temperature as low as 808°C. Second, the sharp breaks in the weight loss versus time plots for the pyrolysis of the North Dakota lignite at times up to 1 s are characteristic of two independent parallel reactions. As just discussed

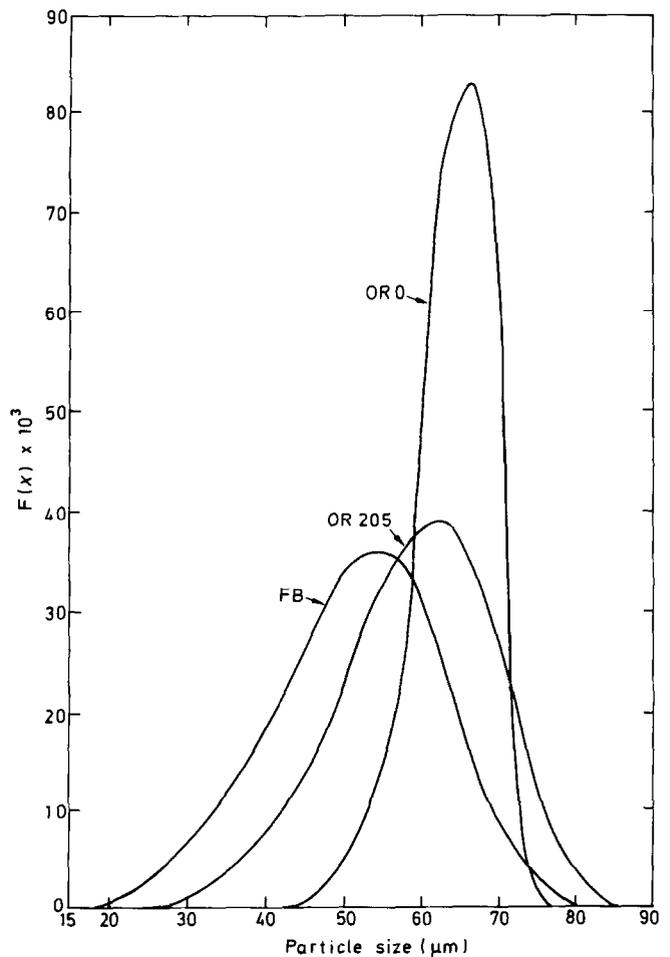


Figure 7 Rosin-Rammler distribution functions for 200 x 270 mesh PSOC-246 coal and chars produced therefrom. (For case nos., see Table 3)

these two reactions are thought to be: (1) the more rapid release of volatile matter coming primarily from the breakdown of carbonyl, carboxyl, hydroxyl, lactone, and methyl groups at the periphery of hydroaromatic and aromatic building blocks; and (2) the less rapid release of volatile matter coming primarily from hydrogen produced during the conversion of hydroaromatic groups to aromatic groups and then to small carbon crystallites. Significantly, the first reaction leads almost entirely to volatile matter, with the production of little carbon (residual char). The second reaction, on the other hand, leads to significant amounts of carbon (residual char) as well as volatile matter. The relative amounts of volatile matter and char produced by the second reaction are a function of the chemical nature of the hydroaromatic and aromatic building blocks in the original coal (that is their size and shape, and hence, C/H ratio) and pyrolysis conditions.

From a kinetic treatment of the weight-loss results which is presented elsewhere³, it is concluded that the apparent activation energy for the release of volatile matter via the rapid removal of functional groups has a minimum value of 230 kJ/mol. This conclusion was based on assuming a reasonable frequency factor of 10^{13} s^{-1} and knowing that insignificant devolatilization occurred during the 95 ms heat-up time to the pyrolysis temperature of 808°C. Limited experimental results appear to be available in the literature giving activation energies for the thermal removal of functional groups from hydroaromatic or aromatic building blocks. It is expected that values will vary widely depending upon the particular functional group and the nature of the building blocks from which it is released. Strange and Walker conclude that the removal of the carbonyl group from graphite, as carbon monoxide, requires an activation energy of 363 kJ/mol¹³.

To the authors' knowledge, activation energy values are also not available for the breakage of crosslinks between the building blocks in coal. These crosslinks are typically ether oxygen, sulphur and methylene groups; oxygen is thought to be the major cross link in lignites. Limited kinetic data are available for the reaction sequence involving the conversion of small aromatic molecules to larger aromatic molecules, to small carbon crystallites, and then larger carbon crystallites. For example, Whang *et al.* report an activation energy of 190 kJ/mol and a frequency factor of $2.6 \times 10^9 \text{ s}^{-1}$ for the conversion of anthracene to larger aromatics at a pressure of 34 MPa¹⁴. There is general agreement that the process of carbon crystallite growth has an activation energy of about 960 kJ/mol¹⁵.

In these studies, pyrolysis yielded chars showing substantially higher open-pore volumes and surface areas than those contained in the precursor lignites. Clearly, the production of additional pore volume created by volatile matter release was dominant over the loss of pore volume due to enhanced building-block alignment and growth. From our limited knowledge on the kinetics of these processes, this is expected to be the case at low pyrolysis temperatures. As pyrolysis temperature is increased, however, building-block alignment and growth become increasingly more significant, leading eventually to chars having lower pore volumes and surface areas than the precursor coals^{11,12}.

It should be noted that, for all samples, surface areas as calculated from nitrogen adsorption at 77 K were significantly lower than those calculated from carbon dioxide adsorption at 298 K. As discussed previously, this is caused by molecular sieving¹⁶. The sieving between nitrogen and carbon dioxide means that the precursor lignites and their chars con-

tain a large concentration of apertures between about 0.49 and 0.52 nm in thickness¹⁶.

Our findings on the differences in chars produced following slow and rapid heating to the same maximum temperature are thought to be significant. Rapid heating yields chars of larger open-pore volumes. Surface-area differences between chars produced by rapid and slow heating are particularly interesting in that those reported in the latter case are higher. This result is now thought to be due to molecular sieving effects. That is, following these studies it has been shown in this laboratory that the surface areas measured on chars increase sharply with increasing outgassing temperature used prior to adsorption runs. Outgassing removes the oxygen complex, formed upon exposure of the chars to the atmosphere and resulting in the blocking of micropores. Ashu has recently shown that if the chars are outgassed at 500°C, both the N₂ and CO₂ surface areas of the samples produced by rapid heating are higher than those by slow heating¹⁷. This reversal in surface areas (produced by differences in outgassing temperature) suggests strongly that the chars produced by rapid heating chemisorb larger amounts of oxygen upon exposure to air at ambient temperatures.

Rapid heating also retards the extent of particle contraction, which all organically-based thermosetting materials undergo more or less upon their pyrolysis. The result is a char particle of lower density and of more accessible pore volume. It would be expected that such particles would exhibit higher reactivity during their gasification. Such has been shown recently by Ashu *et al.* to be the case for 800°C chars derived from lignite PSOC-246 and reacted in air at 500°C¹⁷. The char produced following rapid heating had a reactivity twice that of the char produced following slow heating. This finding clearly gives us another variable, along with selection of precursor coal and HTT, to use in controlling the reactivities of chars produced upon coal pyrolysis.

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