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Physical characteristics of charcoal for use in gunpowder

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A series of experiments are described which identify those characteristics of charcoals which are important for gunpowder manufacture. Charcoals from Alder Buckthorn, Alder, Beech and Douglas Fir woods were prepared by carbonization under nitrogen in the heat-treatment temperature range 523 to 1173 K. The charcoals were characterized by elemental analysis, differential thermal analysis, measurement of spontaneous ignition temperature, morphology using scanning electron microscopy, surface-area assessment using carbon dioxide as adsorbate, mercury porosimetry and microstrength analyses. Results indicate that for charcoals with acceptable carbon contents of 70 to 80 wt %, extremely fine control of carbonization conditions is required. The surface area and carbon content of the charcoal increased rapidly on heat treatment. The surface area of the charcoal reached values of $-400\,m^2\,g^{-1}$. Mercury porosimetry indicated that Alder Buckthorn and Douglas Fir charcoals had cumulative pore volumes greater than Alder charcoal and substantially greater than Beech charcoal. The Beech charcoal was the most friable of the three hardwood charcoals tested using microstrength analysis. Alder Buckthorn and Alder charcoals are recommended for gunpowder manufacture.

1. Introduction

Gunpowder is still used in many weapon systems, from a filling in gun primers to ignite gun propellants, to the role of propellant itself in pyrotechnic signal cartridges. As the cost of replacing gunpowder with other materials in existing armament systems is extremely high, it is therefore likely that, because of its versatility and low cost gunpowder will continue to be used well into the 21st century [1]. In order to ensure a continuing supply of suitable material, it is important to gain a fuller understanding of those parameters which influence the ignition and burning of gunpowder.

A number of investigators have attempted to identify those factors which affect the combustion of gunpowder [2–5] and interest has been shown in the role of charcoal in the combustion process. Blackwood and Bowden [2] maintained that the presence of volatile "oxyhydrocarbons" in charcoal was essential for ignition to succeed. Douillet [3] examined the influence of volatile matter content of characterized charcoals on the performance of gunpowders prepared from charcoals. He concluded that the rate of burning of gunpowder increased with the proportion of volatile matter. Urbanski *et al.* [6, 7] examined the chemical changes occurring during the carbonization of the constituents of wood and proposed that the presence of free radicals in charcoal was important in the combustion of gunpowder [8]. Hintze [9] prepared mixtures of wood charcoal, sulphur and potassium nitrate in the laboratory using charcoals with a range of carbon contents, but of unspecified origins. He concluded that materials with carbon contents between 78 and 82% produced the best gunpowders. However, he did not verify these

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conclusions with trials in stores. Porter and Stimson [10] on the other hand, found that when various Alder charcoals were manufactured into gunpowder the materials with a carbon content of approximately 72% gave the fastest burning powder. Kirshenbaum [11] also examined mixtures produced using a variety of charcoals including materials from mineral sources, and proposed that powders prepared using carbons with high volatile contents had lower activation energies and temperatures of ignition than those prepared using carbons with low volatile contents.

Since charcoal for gunpowder is manufactured from naturally occurring resources, its properties can vary depending upon the species of the parent wood from which it is prepared, the growing conditions and age of the tree used and the method of carbonization of the wood. In the United Kingdom until 1976, gunpowder was generally produced using charcoal prepared from Alder Buckthorn (sometimes erroneously named dogwood), Alder or Willow. The current MOD specification for charcoal type A [12] permits only the woods of these trees. Some Victorian writers [13, 14] claimed that no other native woods produced powders of equivalent quality and more recent workers confirmed that gunpowder containing Beech charcoal was unsuitable for use in UK armaments [10, 15]. Gray *et al.* have reviewed the history of gunpowder and the role of charcoal in its manufacture [16].

The purpose of this report is to describe a series of experiments which was carried out to identify the characteristics of charcoals which affect its role in gunpowder. The two charcoals which are recommended for use in gunpowder manufacture for fuzes (Alder Buckthorn and Alder) were compared in a series of tests with two which are unacceptable (Beech and Douglas Fir). Charcoals were prepared by the carbonization of the four woods at various temperatures and the physical structures of the resulting materials were examined using scanning electron microscopy (SEM). The charcoals were characterized by elemental analyses, by surface area and physical strength measurements and by assessments of their behaviour under thermal analysis.

2. Experimental details

2.1. Materials

Four types of wood were used in this study and these are listed below along with the location at which each was collected. The Douglas Fir is a softwood, the others being hardwoods.

Alder Buckthorn (Frangula alnus)	Wicken Fen, Cambridgeshire
Alder (Alnus glutinosa)	Kielder Forest, Northumberland
Beech (Fagus sylvatica)	Chopwell Forest, Northumberland
Douglas Fir (Pseudotsuga menziesii)	Chopwell Forest, Northumberland

Freshly cut wood was debarked immediately. Weathered wood had to be boiled in water for severel hours until the bark was softened sufficiently for removal. The wood was then left to dry for several weeks in warm, well-aired conditions before being cut into pieces approximately 150 mm in length and 30 mm in diameter for carbonization.

2.2. Carbonization of woods

Samples of wood in silica boats were carbonized, under flowing nitrogen, in a Carbolite horizontal tube furnace. The furnace was heated from cold at a rate of 3 K min^{-1} to a pre-determined heat-treatment temperature (HTT) between 523 and 1173 K. This temperature was maintained with a precision of 1 K for a soak time of between 0 and 24 h from the time when the desired temperature was first attained. The large quantities of volatile materials released during the carbonization process were collected in a cold trap located at the outlet from the furnace. At the end of the soak period, the charcoal was allowed to cool for at least 16 h inside the furnace under the nitrogen flow and was then transferred to an airtight tin for at least one week until the risk of spontaneous ignition in air had passed.

2.3. Elemental analysis

Charcoals prepared in the furnace were analysed for carbon, hydrogen, nitrogen and ash content using a Perkin Elmer 240B analyser and results are quoted on a dry basis.

2.4. Differential thermal analysis

The thermal decomposition of wood under a stream of nitrogen was examined gravimetrically in an STA780 simultaneous thermal analyser using a heating rate of 18 K min^{-1}.

2.5. Thermogravimetric examination of oxidation of charcoal

Charcoal samples were prepared by heating the parent wood at 18 K min^{-1} to a predetermined HTT for 3 h in the furnace of the STA780 instrument under flowing nitrogen. After completion of this process, the charcoal sample was left to cool *in situ* under nitrogen. Air was then admitted to the furnace which was heated at a rate of 18 K min^{-1} and the thermo-gravimetric analysis (TGA) plot was recorded along with the corresponding differential (DTG) curve. "Spontaneous ignition temperature" (SIT), defined as the temperature at which the onset of rapid weight loss occurred, was determined by extrapolating the leading slope of the DTG curve back to the temperature axis.

2.6. Scanning electron microscopy

The structures of charcoals were examined using a Cambridge Stereoscan Mk IIA scanning electron microscope (SEM). Samples of charcoals were cut using a scalpel in the form of small cubes of side 3 mm. These cubes were mounted on SEM stubs and vacuum-coated with carbon and gold to reduce charging of the specimen and enable a good image to be obtained.

2.7. Surface area measurements

Apparent surface areas were determined for a series of charcoals by the adsorption of carbon dioxide at 195 K on to samples of charcoal, 0.3 g in weight, in a McBain-spring gravimetric gas adsorption apparatus. The samples were outgassed by evacuating the system to a pressure of < 1.3 mPa and heating the sample at 373 K using boiling water until no further weight loss as determined by the extension in the spring was observed. Assuming monolayer coverage at 20 kPa of carbon dioxide, a "one-point" method of surface area assessment was adopted [17]. Extents of adsorption were measured by admitting carbon dioxide at 20 kPa and 195 K to the outgassed sample and by monitoring the change in weight of the sample over 24 h. The apparent surface area was then calculated using Equation 1:

$$s = x_{\mathrm{m}} A_{\mathrm{m}} L \tag{1}$$

where s is the surface area (m^{2}g^{-1}), x_{m} the number of moles of CO_2 adsorbed per unit weight of adsorbent (mol g^{-1}) at 20 kPa pressure, A_{m} the apparent cross-sectional area of CO_2 molecule (0.17×10^{-18} m^2), and L Avogadro's number (6.02×10^{23} mol^{-1}).

2.8. Mercury porosimetry

Mercury porosimetry was carried out using a Carlo Erba model 200 porosimeter using pressures between 0.1 and 200 MPa, measuring volumes of pores with radii of entrance from 7.5 μm to 3.7 nm. Because of the possibility of damage to the specimen caused by mercury intrusion [18], the extent of such damage was assessed by testing a set of charcoal samples HTT 573 K. Mercury was removed from these samples by heating them to 573 K under vacuum until their weights had returned to their original values and then re-testing the samples by mercury porosimetry. The results of the first and second impregnation were compared to assess any change in porosity caused by repeated mercury intrusion and removal.

2.9. Microstrength analysis

Microstrength testing of charcoals was carried out using the apparatus proposed by Riley [19]. Charcoals carbonized at 573 K were prepared for testing by crushing them using a pestle and mortar and then sieving them (using a sieve shaker) to provide test specimens with particles in the size range 600 to 1.18 μm. A 2 g sample of the test specimen was placed in a steel tube of length 305 mm and diameter 25 mm containing twelve ball bearings of 8 mm diameter. The tube was sealed and then rotated about its centre in the plane of its main axis for 8 min at 25 rpm, the speed at which the ball bearings fall the full length of the tube, crushing the material inside. After crushing, each sample was sieved into three fractions: material retained on a 600 μm sieve: material passing a 600 μm sieve but retained on a 212 μm sieve: and material passing a 212 μm sieve. The fractions were weighed to obtain a strength analysis.

After sieving, each fraction was examined using SEM and the aspect ratios (ratio of length of the longest chord of a particle to the maximum dimension of the particle in a direction perpendicular to the longest chord) of 300 particles were measured by examining a two-dimensional image of particles resting in their most stable positions.

3. Results and discussion

3.1. Elemental analysis

Results obtained for Alder charcoals prepared using various soak times at each of three temperatures (523, 573, 593 K) are shown in Table I. There is an initial rapid rise in carbon content during the time taken to reach the HTT and the first hour of

TABLE I Elemental analyses of Alder charcoals

Carbonization Temperature (K)	Soak Time (h)	Elemental analysis (wt %, dry basis)			
		Carbon	Hydrogen	Nitrogen	Ash
Wood		50.6	5.80	0.21	0.27
523	0	52.9	5.54	0.08	0.47
523	1	56.2	5.95	0.23	1.62
523	2	56.5	5.84	0.43	0.78
523	3	57.3	6.00	0.42	0.40
523	12	59.6	5.78	0.45	0.45
523	24	60.5	5.70	0.41	0.45
573	0	71.9	4.64	0.38	0.83
573	1	74.2	4.79	0.39	0.86
573	2	75.0	4.64	0.27	0.92
573	3	74.1	4.73	0.38	0.45
573	12	76.5	4.49	0.37	1.04
573	24	77.2	4.50	0.04	1.20
593	0	74.6	4.64	0.53	0.54
593	1	74.6	4.72	0.56	0.56
593	2	74.3	4.71	0.53	0.52
593	3	74.6	4.13	0.60	1.02
593	12	75.6	4.33	0.61	0.79
593	24	76.2	4.53	0.56	0.73

soak. After this the rate of increase in carbon content with soak time is slow, indicating that the carbonization process is continuing but at a reduced rate. In order to standardize the specimens, all remaining carbonizations were carried out using standard soak periods of 3 h. Results obtained for the charcoals prepared from each of the parent woods subjected to various HTTs for 3 h soak are shown in Table II (Alder Buckthorn), III (Alder), IV (Beech) and V (Douglas Fir). Fig. 1 is a plot of the results for Alder charcoal tabulated in Table III.

All the hardwoods showed similar increases in

TABLE II Elemental analyses of Alder Buckthorn Charcoals (3 h soak)

Carbonization Temperature (K)	Elemental analysis (wt %, dry basis)			
	Carbon	Hydrogen	Nitrogen	Ash
Wood	50.6	5.92	0.07	0.32
523	53.9	5.91	0.16	0.57
533	55.5	5.73	0.27	0.53
548	53.2	5.66	0.19	0.53
553	57.8	5.63	0.13	0.60
573	69.7	5.04	0.19	0.90
593	75.2	4.40	0.30	0.94
598	76.1	4.87	0.20	0.78
623	78.0	4.27	0.34	0.94
648	80.4	4.28	0.14	0.97
673	81.7	4.11	0.19	1.58
723	86.3	3.73	0.19	1.07
773	89.0	3.16	0.16	1.10
823	93.6	2.97	0.18	2.39
873	93.7	2.55	0.18	2.56
923	95.2	1.94	0.09	0.77
973	96.4	1.53	0.08	0.87
1023	96.9	1.30	0.10	1.03
1073	96.0	1.13	0.05	0.97
1123	96.5	1.02	0.03	1.59
1173	95.7	0.86	0.43	1.14

TABLE III Elemental analysis of Alder charcoals (3 h soak)

Carbonization temperature (K)	Element analysis (wt %, dry basis)			
	Carbon	Hydrogen	Nitrogen	Ash
Wood	50.6	5.80	0.21	0.27
523	53.9	5.91	0.16	0.57
533	55.5	5.73	0.27	0.53
548	58.0	5.66	0.35	0.41
553	61.7	5.51	0.38	0.35
563	68.9	5.09	0.51	0.53
573	71.6	4.96	0.21	0.74
583	74.1	4.69	0.42	0.62
593	74.7	4.82	0.48	0.54
623	78.1	4.29	0.66	0.52
653	79.1	4.34	0.52	1.00
673	83.5	3.69	0.44	0.72
723	86.9	3.58	0.46	0.65
773	89.9	3.17	0.57	1.14
823	93.7	2.71	0.81	0.97
873	94.9	2.52	0.60	1.29
923	94.0	1.84	0.46	0.71
983	96.4	1.56	0.23	1.22
1023	95.5	1.20	0.39	1.01
1073	96.3	1.18	0.26	0.95
1123	93.6	1.35	0.24	1.40
1173	96.8	1.25	0.80	1.44

carbon content with HTT. Below 523 K there was little change in carbon content with HTT, but between 523 and 623 K the carbon content increased rapidly from 54 to 78%. The rate of increase in carbon content then diminished until it became very low at 95% carbon content (873 K). The decrease in hydrogen content reflected closely the carbon content profile.

TABLE IV Elemental analyses of Beech charcoals (3 h soak)

Carbonization temperature (K)	Element analysis (wt %, dry basis)			
	Carbon	Hydrogen	Nitrogen	Ash
Wood	49.4	6.03	0.03	0.46
523	53.4	5.76	0.20	0.56
533	54.0	5.50	0.22	0.42
548	56.2	5.68	0.17	0.27
553	66.0	5.03	0.22	0.37
563	70.6	4.94	0.25	0.41
573	70.9	4.88	0.29	0.88
593	74.4	4.63	0.30	0.92
623	77.0	4.09	0.33	0.66
648	80.4	4.09	0.34	0.86
658	81.3	4.05	0.32	0.96
673	80.5	4.04	0.32	0.88
748	88.5	3.09	0.73	1.04
873	95.7	2.54	0.60	1.29
923	94.0	1.84	0.46	0.71
973	94.7	1.53	0.08	0.87
1023	95.5	1.20	0.39	1.01
1123	95.5	1.13	–	1.45
1173	96.8	1.11	0.04	1.46

TABLE V Elemental analysis of Douglas Fir charcoals (3 h soak)

Carbonization temperature (K)	Element analysis (wt %, dry basis)			
	Carbon	Hydrogen	Nitrogen	Ash
Wood	50.1	6.08	–	0.44
523	57.1	5.81	–	0.58
558	69.7	5.38	0.43	1.85
573	72.9	5.06	0.10	0.43
598	75.1	5.31	0.20	0.31
603	76.2	5.26	0.19	0.41
613	76.8	5.08	0.28	0.33
663	80.3	4.36	0.08	0.41
673	82.4	3.87	0.17	0.57
723	84.6	3.75	0.09	0.31
1073	98.1	1.19	–	0.38
1173	96.8	1.11	–	1.46

Although the shape of the curve for Douglas Fir, a softwood, was similar to those of the hardwood curves, the rapid increase in carbon content occurred over the slightly lower temperature range of 475 to 600 K.

It is apparent from Fig. 1 and Tables II to V that the range of carbon contents (70 to 80%) traditionally required for charcoal for gunpowder [12] is difficult to achieve because it occurs in the

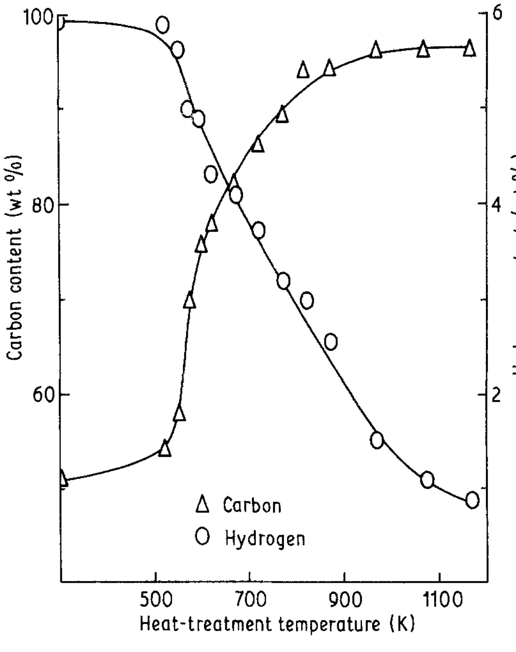


Figure 1 Variation of carbon and hydrogen contents with HTT for charcoals prepared from Alder wood.

region of rapid increase in carbon content with HTT. A small change in HTT could affect the final carbon content of charcoal quite dramatically in this the required range.

3.2. Differential thermal analysis

A typical trace for Alder Buckthorn wood is shown in Fig. 2. This trace had endotherms centered on 373, 500 and 600 K and comparison of this trace with those provided by samples of reference materials indicated that the peaks could be assigned as follows:

373 K	vaporization of water
500 K	decomposition of lignin
600 K	decomposition of cellulose

The wood cell wall is composed mainly of polymeric substances (primary components) and smaller quantities of lower molecular weight organic compounds and inorganic compounds (extraneous materials). Most of the low molecular weight organic compounds, such as polyphenols, can be extracted using organic solvents or by steam distillation [20], leaving behind a small quantity of inorganic mineral matter as well as the primary components cellulose, hemicellulose and lignins [21]. Wood cellulose, which constitutes 40 to 50% of the cell wall, has a chain length of approximately 10,000 units and hemicellulose, which is a mixture of polysaccharides formed by the polymerization of various sugars [22], constitutes 20 to 35% of the wall. Lignin is an amorphous substance which imparts increased rigidity to the cell wall and is present in proportions varying between 15 and 33%: it is believed to be a polymer whose basic structural unit is a propylphenol substituted with between one and three methoxy groups [23].

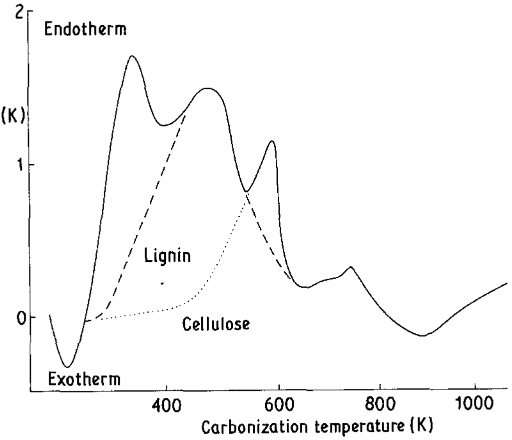


Figure 2 The DTA curve for carbonization of Alder Buckthorn wood under nitrogen; heating rate 18 K min^{-1}.

It is likely, therefore, that the rapid increase in carbon content commencing at 523 K during the carbonization process is caused by the decomposition of lignin and partial decomposition of polysaccharides to carbon and tars and subsequent volatilization of the tars.

3.3. Thermogravimetric examination of oxidation of charcoal

This examination of three charcoals (Alder Buckthorn, Alder and Beech) yielded the results listed in Table VI. The plot of SIT against HTT for Alder Buckthorn is typical of the three woods and is shown in Fig. 3: the most obvious feature of this plot is its minimum at approximately 550 K. Comparison of the curve with Figs. 1 and 2 shows that this feature occurred in the region of rapid increase in carbon content and also in the region where extensive decomposition of lignin and onset of decomposition of cellulose would be expected. The maximum in the curve occurred at an HTT of 548 K and the minimum at 573 K, corresponding to carbon contents of approximately 57.5% and 70%.

At sufficiently low HTT, e.g. 400 K, the only change taking place under nitrogen was loss of water: when a sample treated at this temperature

TABLE VI Variation of SIT with HTT for selected charcoals

HTT (K)	SIT (K)		
	Alder Buckthorn	Alder	Beech
298	478	496	499
388	483		493
396		491	
478	498		
497		498	506
526		521	530
538	523	489	547
548	538		
553		518	526
573	503	515	538
620			536
625		538	
673	538	561	583
773	573	605	600
803		613	
873	588	623	613
943	603		
968		633	
1073	633	643	618

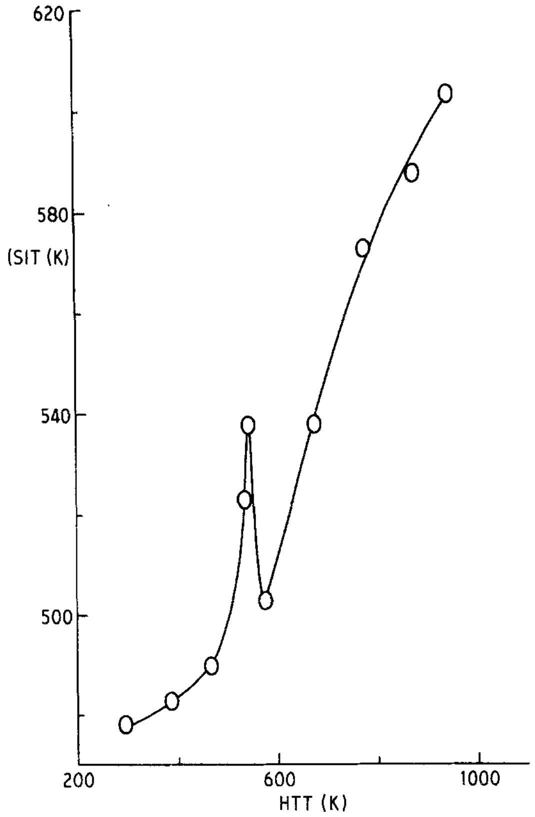


Figure 3 Variation of SIT with HTT for charcoals prepared from Alder Buckthorn wood.

was subsequently heated in air, the initial rapid weight loss observed at 483 K was probably due not to ignition but to the onset of decomposition of lignin and the volatilization of some materials of low molecular weight. At a higher HTT of 550 K, the changes occurring on heating in nitrogen would be loss of water, extensive decomposition of lignin and partial decomposition of cellulose as well as volatilization of low molecular weight materials: the sample reheated in air showed an SIT of 538 K indicating that interaction with atmospheric oxygen was occurring. At an HTT of 560 K the changes taking place under nitrogen were unlikely to be very different from those occurring at 550 K but in a sample treated in this way there was a rapid drop in SIT. Since this drop could not be due to a simple decomposition of the lignin or cellulose (such would have occurred already under nitrogen) or to the oxidation of these materials (this would have occurred more readily in material pre-treated at lower HTTs), it must have been caused by one or both of the following processes:

1. further decomposition and subsequent volatilization of initial products of decomposition;
2. oxidation of non-volatile products of decomposition.

This indicates that initial products of decomposition were at a maximum at 573 K, corresponding to a carbon content of 70% and is in agreement with the conclusion of Porter and Stimson [10]. At HTTs of 700 K and higher, more of the wood sugars and carbohydrates would decompose to volatile products and be driven off in the nitrogen stream. Therefore a rapid increase of SIT in air was observed as a progressively smaller proportion of the sugars and non-volatile products remained available for reaction with oxygen, and SIT approached the temperature of ignition of carbon in air.

In an attempt to identify the products of decomposition which are present in charcoals, experiments were carrived out [24] to extract charcoal samples in a Soxhlet apparatus using either pyridine or acetone as solvent and the results of these experiments are reproduced in Table VII. The extract from Alder charcoal was examined using a GC/MS technique and gave more than 100 peaks on the GC. Five of the major peaks were identified as members of an homologous series of dibenzofurans monosubstituted in the 8-position. These results indicated that most of the material which is volatile at high temperatures must be chemically bound to the charcoal or else trapped in the pore structure. They were in sharp contrast to those of Blackwood and Bowden [2], who emphasized the importance of extractable organic materials in charcoal on the ignition of gunpowder.

TABLE VII Solvent extractable material in charcoals

Charcoal	Carbon (%)	Soluble matter in	
		Actone (%)	Pyridine (%)
Alder	81.7	0.23	0.78
	80.5	0.31	1.03
	77.6	0.32	2.37
	77.0	0.76	2.20
	76.3	1.19	2.16
	74.0	1.97	5.17
	58.4	4.09	8.14
Alder Buckthorn	59.0	3.32	10.02
Oak	78.1	0.32	1.18
Maple	78.0	0.64	2.22

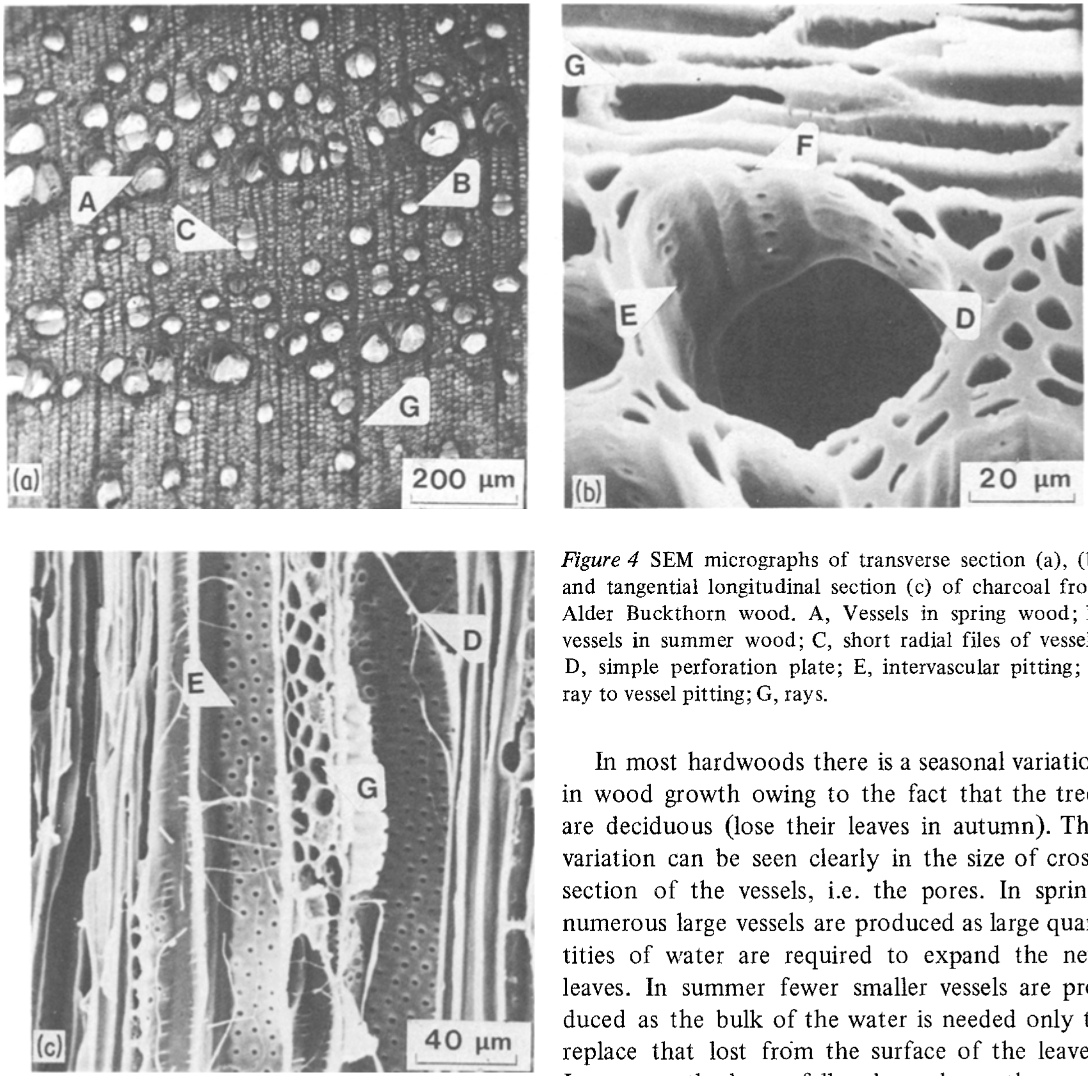


Figure 4 SEM micrographs of transverse section (a), (b) and tangential longitudinal section (c) of charcoal from Alder Buckthorn wood. A, Vessels in spring wood; B, vessels in summer wood; C, short radial files of vessels; D, simple perforation plate; E, intervascular pitting; F, ray to vessel pitting; G, rays.

3.4. Scanning electron microscopy

Electron micrographs of Alder Buckthorn, Alder, Beech and Douglas Fir charcoals are shown in transverse and tangential longitudinal section in Figs. 4 to 7, respectively. In such isotropic materials, the macromorphology is derived from the biological structure of the parent wood and, although some shrinkage and distortion occurs, the anatomy of the charcoal is essentially a shrunken pseudomorph of the parent material. It can, therefore, be identified by its unique structure [25, 26].

(a) Hardwoods. Hardwoods possess vessels. These are a tube-like series of longitudinally aligned cells joined axially by perforation plates in the cell and walls. The primary purpose of the vessels is water transport, the older lignified vessels also giving the wood strength.

In most hardwoods there is a seasonal variation in wood growth owing to the fact that the trees are deciduous (lose their leaves in autumn). This variation can be seen clearly in the size of cross-section of the vessels, i.e. the pores. In spring, numerous large vessels are produced as large quantities of water are required to expand the new leaves. In summer fewer smaller vessels are produced as the bulk of the water is needed only to replace that lost from the surface of the leaves. In autumn the leaves fall and wood growth ceases. This pattern can be clearly seen in the wood. The age of a deciduous hardwood can be determined by counting the number of annual rings in the wood indicating the large spring growth pores.

Hardwoods also possess ray cells. These cells run radially out from the centre of the wood and are used mainly for food transport and storage.

(b) Softwoods. Softwoods are composed of tracheids. These cells unlike the hardwood vessels are square in cross-section and have tapered overlapping ends. These are the water transport system of the softwoods. Most softwoods are not deciduous and there is no distinct variation in tracheid size throughout the year. Softwoods may show growth rings owing to slow winter growth caused by severe climatic conditions.

Ray tissue is also present in softwood and is used for food storage and transport.

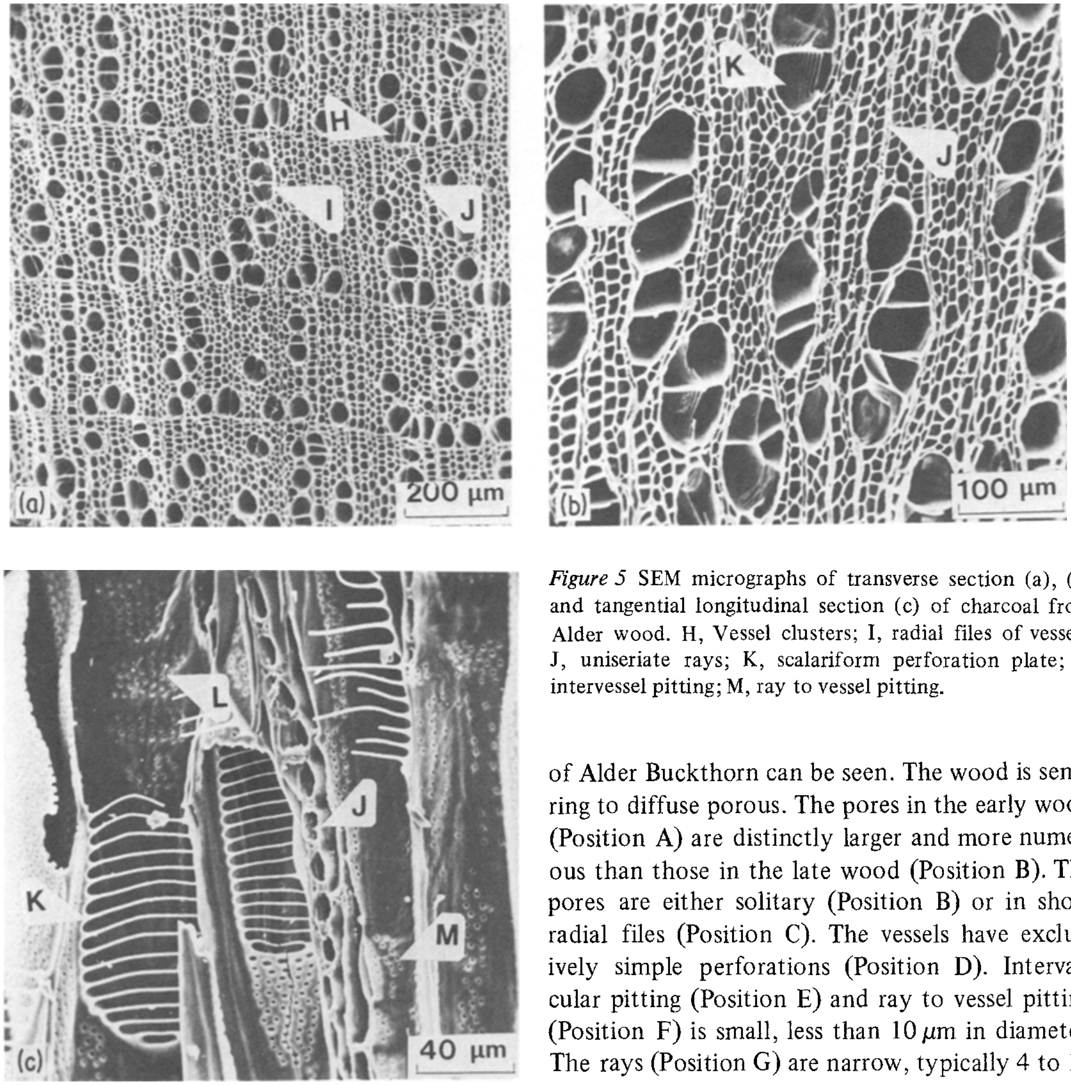


Figure 5 SEM micrographs of transverse section (a), (b) and tangential longitudinal section (c) of charcoal from Alder wood. H, Vessel clusters; I, radial files of vessels; J, uniseriate rays; K, scalariform perforation plate; L, intervessel pitting; M, ray to vessel pitting.

Softwoods possess resin canals. These are not found in hardwoods. Soft bodied cells secrete resin into the canal to be transported throughout the wood.

Woods have unique structures and can be identified by the presence or absence of various anatomical features.

The micrographs of the specimens examined were compared with examples provided in the literature and are described below [21]. Because the specimens were prepared almost exclusively from branch wood rather than trunk wood, not all of the characteristic features of each of the woods were necessarily observed.

3.4.1. Alder Buckthorn (Fig. 4)

In the transverse section the characteristic features of Alder Buckthorn can be seen. The wood is semiring to diffuse porous. The pores in the early wood (Position A) are distinctly larger and more numerous than those in the late wood (Position B). The pores are either solitary (Position B) or in short radial files (Position C). The vessels have exclusively simple perforations (Position D). Intervascular pitting (Position E) and ray to vessel pitting (Position F) is small, less than 10 μm in diameter. The rays (Position G) are narrow, typically 4 to 10 cells wide.

In tangential longitudinal section the simple perforation plates (Position D) can be clearly seen in cross-section. Greater detail of the rays can be seen in longitudinal section. The ray tissue is homogeneous, the cells appearing oval in axial section (Position G). The rays are principally bi- and triseriate, uniseriate rays being rare. The vessel-to-vessel pitting is small, less than 10 μm (Position E).

3.4.2. Alder (Fig. 5)

In transverse section, clusters of vessels can be seen in the early wood (Position H). The pores are radially orientated, radial pore multiples being common (Position I). The rays are exclusively uniseriate (Position J). The perforation plates are scalariform (Position K). The scalariform perforation plate can be seen to be formed by the deterioration of two adjacent cell walls. The vessel-

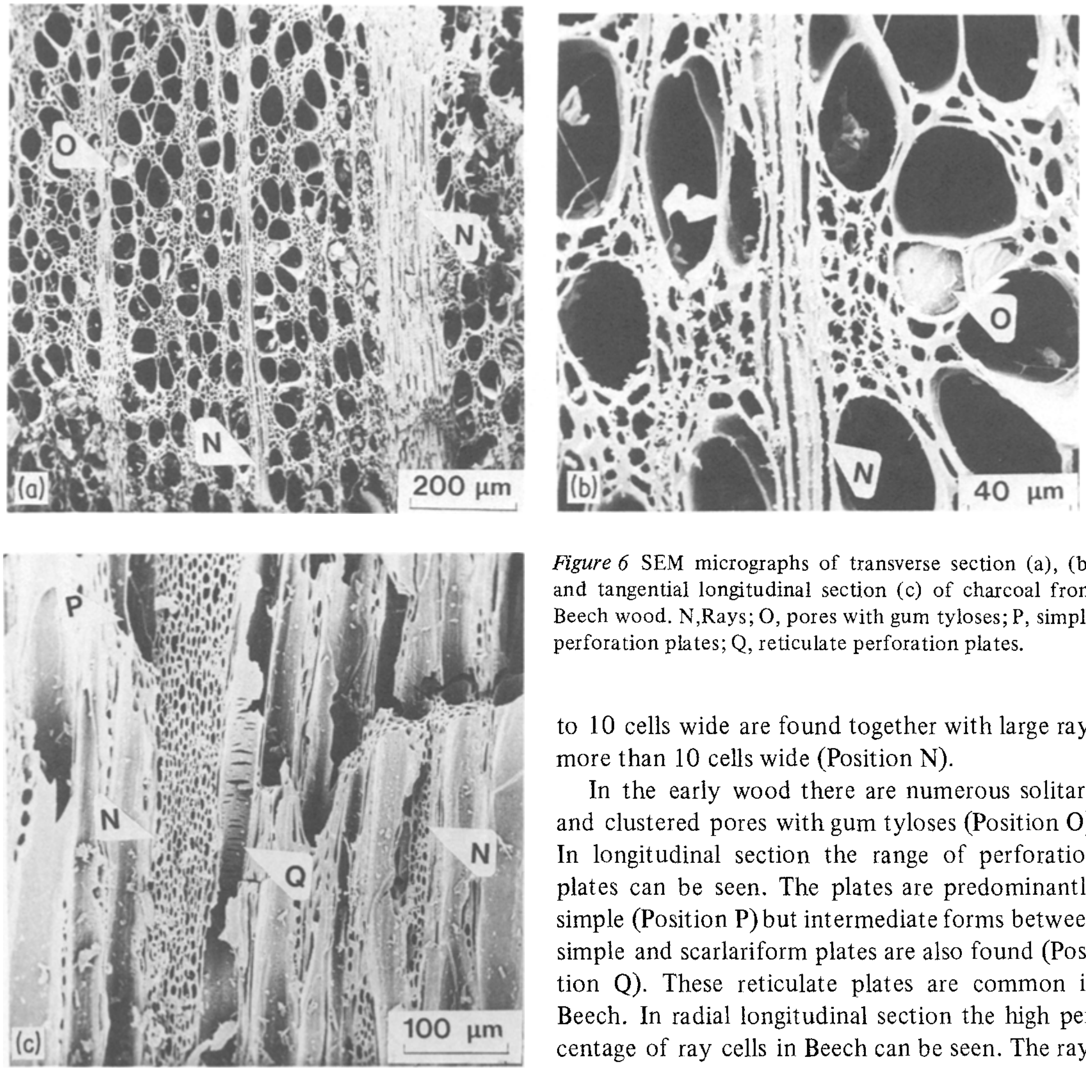


Figure 6 SEM micrographs of transverse section (a), (b) and tangential longitudinal section (c) of charcoal from Beech wood. N, Rays; O, pores with gum tyloses; P, simple perforation plates; Q, reticulate perforation plates.

to vessel pitting is small, less than 10 μm in diameter (Position L).

In longitudinal section the scarlariform perforation plates can be seen more clearly. The plates usually have between 10 and 20 bars (Position K). The rays can be seen to be homogeneous, the ray cells being oval in axial view (Position J). The intervessel pitting is fine, less than 10 μm in diameter (Position L) and similar in size to the ray to vessel pitting (Position M).

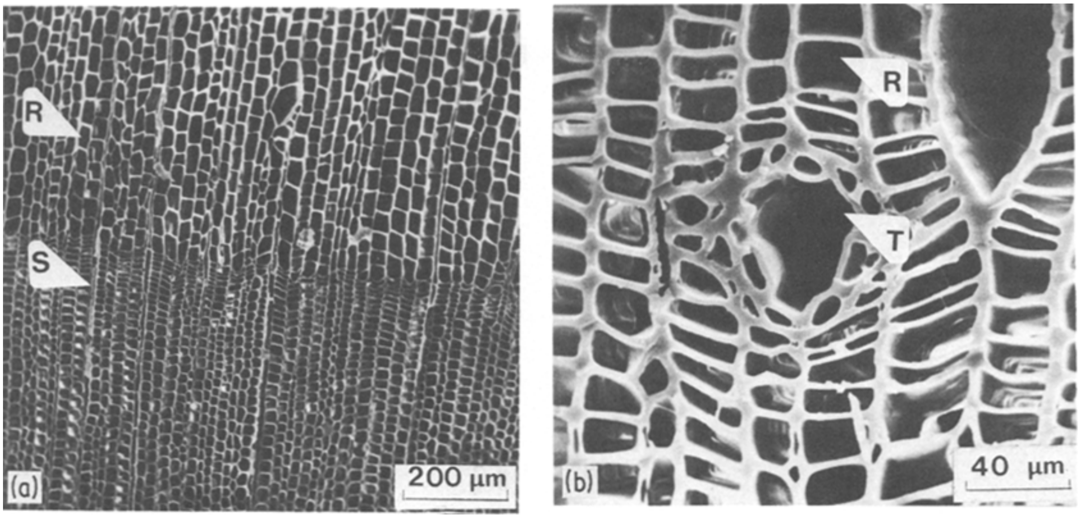
3.4.3. Beech (Fig. 6)

Beech can be distinguished from the other two hardwoods easily in a hand specimen owing to the presence of very large rays. In transverse section the variation in ray size can be seen. Small rays 4 to 10 cells wide are found together with large rays more than 10 cells wide (Position N).

In the early wood there are numerous solitary and clustered pores with gum tyloses (Position O). In longitudinal section the range of perforation plates can be seen. The plates are predominantly simple (Position P) but intermediate forms between simple and scarlariform plates are also found (Position Q). These reticulate plates are common in Beech. In radial longitudinal section the high percentage of ray cells in Beech can be seen. The rays commonly exceed 1 mm in height (Position N). In tangential longitudinal section, the large masses of ray tissue are the most obvious feature (Position N). The rays are homogeneous being composed entirely of thick-walled cells which are oval in axial section.

3.4.4. Douglas Fir (Fig. 7)

The square-shaped cross-section of the tracheids (Position R) and the relatively regular appearance of the rays (Position S) give this wood a very even grain, a characteristic of the softwoods. The rays are between 8 and 15 cells in height. Resin canals which can be either longitudinal (Position T) or transverse (Position U) are comparatively rare and are bordered by 7 to 12 secretory cells. The bordered pits in the tracheids (Position V) can be clearly identified and are approximately 10 μm in diameter.



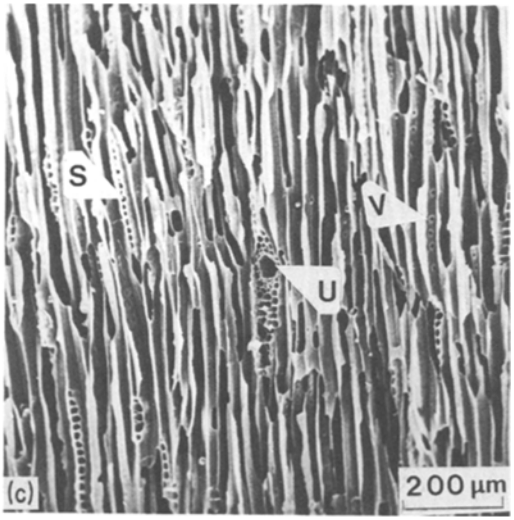


Figure 7 SEM micrographs of transverse section (a), (b) and tangential longitudinal section (c) of charcoal from Douglas Fir wood. R, Tracheids, square-shaped cross-section; S, regular appearance of rays; T, longitudinal resin canals; U, transverse resin canals; V, bored pits of tracheids.

3.5. Surface-area measurements

The variation in apparent surface area with HTT is shown in Table VIII for four different wood charcoals and a plot of the data for Beech charcoal in Fig. 8. The main features of this plot, which resembles those for Alder Buckthorn and Alder, are the rapid increase which takes place in surface area over the range 550 K to 650 K, a point of inflection at approximately 700 K and a subsequent rapid increase. A dip appeared in each of the curves for hardwoods between 870 and 970 K. It is apparent, therefore, that the temperature of the initial rapid rise in surface area of the charcoal coincides with that of the rapid rise in carbon content, as might be expected.

3.6. Mercury porosimetry of charcoals

Pore-size distribution for Alder Buckthorn, Alder and Beech woods and charcoals are shown in Figs. 9 to 11. On carbonization of hardwoods, the number of pores with a given radius of entrance generally increased with HTT and the shapes of the

TABLE VIII Apparent surface areas of charcoals by CO_2 absorption

HTT (K)	Apparent surface area ($m^2\ g^{-1}$)			
	Alder Blackthorn	Alder	Beech	Douglas Fir
548	–	70		
553	20		76	
563		70		
573	120	170	110	140
593		190	170	
598	200			
623		180	230	
648		250	250	
673		280	230	250
723		300	250	
743			300	
773	300	380		
778			340	
823	380	390	350	
873		350	360	
923	360	390	340	
973	380	400	300	
1023		360	380	
1073			400	
1123			430	

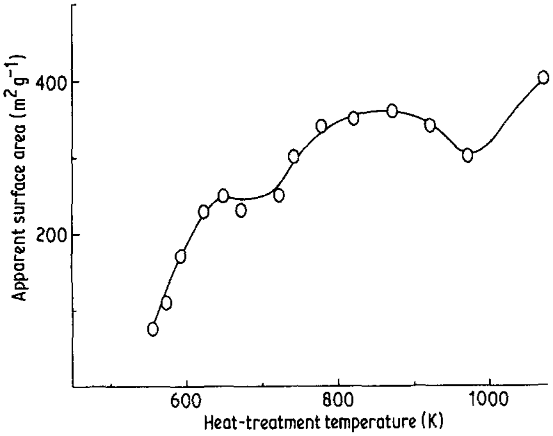


Figure 8 Variation of apparent surface area with HTT for charcoals prepared from Beech wood.

TABLE IX Cumulative pore volumes for various charcoals

HTT (K)	Cumulative pore volume (cm^3 g^{-1})			
	Alder Buckthorn	Alder	Beech	Douglas Fir
Wood	0.94	0.93	0.47	1.35
523	1.20	1.25	0.45	
548	1.49,1.38	1.19	0.36	
553	1.34	1.23	0.49	
573	2.14,2.28	1.44	0.54,0.67	2.41
583		1.26		
593	1.82	1.73	0.67	
623	1.94	1.46	0.91	
648			0.97	

distribution curves for the charcoals were similar to those of the parent woods. However, Douglas Fir charcoal, in which the pore radius was almost exclusively 1.0 μm, differed greatly from the parent wood, which had pores only of radius 100 nm. A list of cumulative pore volumes for all of the woods and charcoals examined is given in Table IX, from which it may be seen that the cumulative pore volume for each wood generally increased with HTT, although some spurious results did not follow the trend.

These results indicated that although there was not a great difference between the cumulative pore volumes for Alder Buckthorn and Alder charcoals at any given temperature, a large number of pores in Alder charcoals had radii of entrance of the order of 1 μm whereas for Alder Buckthorn two ranges of 20 to 100 nm and 300 to 600 nm were apparent. It is significant that the cumulative pore volumes of Beech charcoals were lower than those of the equivalent Alder Buckthorn or Alder charcoals, but again two ranges of 20 to 60 nm and 300 to 600 nm were present.

The experiments to investigate damage by mercury intrusion showed that whereas no significant differences could be observed between first and second runs for Alder or Douglas Fir charcoals, in which most of the pores had radii of entrance of approximately 1.0 μm, damage was caused to Alder Buckthorn (Fig. 12) and to Beech charcoals. The changes in shape of these distribution curves could be attributed almost exclusively to damage to pores with radius of entrance smaller than 100 nm.

3.7. Microstrength analysis and particle shape analysis

The results of the microstrength analysis of three charcoals are shown in Table X and of the particle

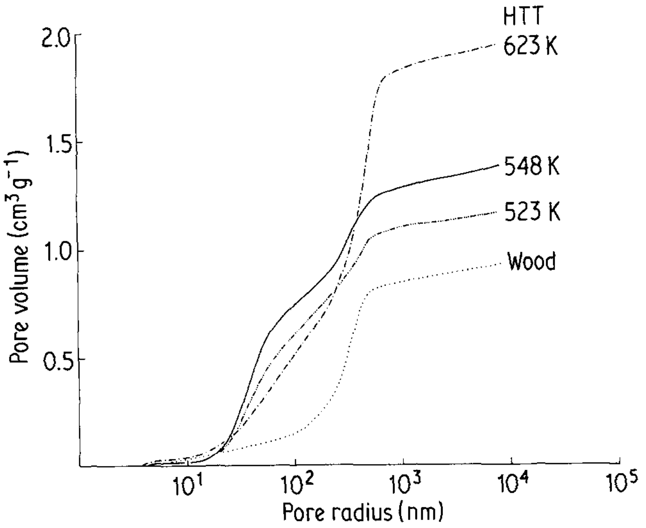


Figure 9 Variation of pore volume with pore radius from mercury porosimetry, for charcoals prepared from Alder Buckthorn wood.

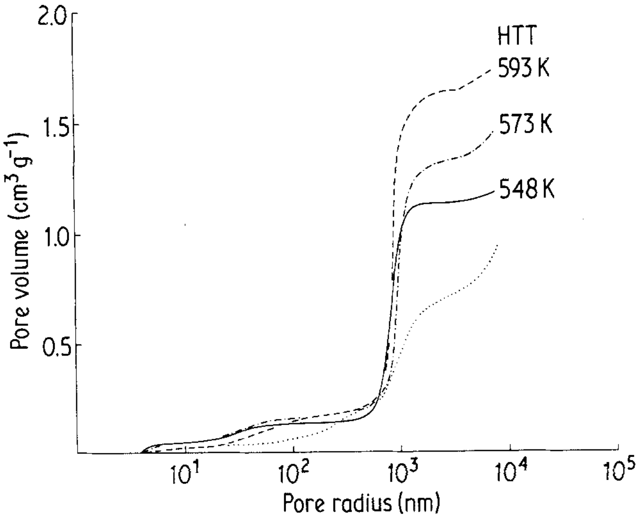


Figure 10 Variation of pore volume with pore radius, from mercury porosimetry, for charcoals prepared from Alder wood.

shape analysis in Table XI. The results of the sieve analysis indicated that Alder Buckthorn charcoal, with the greatest proportion of material retained on the 600 μm sieve, possessed the greatest resistance to crushing and hence the greatest strength of the three charcoals examined. Beech charcoal, with the least material retained on the 600 μm sieve, was the weakest. Particle shape analysis indicated that Alder and Alder Buckthorn tended to fracture in such a way as to produce long splinters, whereas Beech particles were more equi-dimensional. This trend was repeated in the finest fraction although a larger number of splinters of Beech charcoal were observed in this fraction than in the coarser fractions. No results for Douglas Fir were obtained.

It appears from these tests that Beech charcoal was the most friable of those examined and produced the most uniformly shaped particles. This can be readily explained by assuming that ray tissue, which is the weakest portion of the wood, is also the weakest portion of the charcoal. Beech charcoal contains a large proportion of ray tissue in broad rays and so might be expected to break up more readily and more uniformly than Alder Buckthorn or Alder, which possess narrower rays.

To examine further the importance of micro-strength and particle shape of the charcoal, various samples of UK G12 gunpowder were extracted with methylene chloride to remove sulphur and then with water to remove potassium nitrate and the residual charcoals were examined using SEM. All of the particles were in the range 5 to 50 μm but mostly between 5 and 10 μm. The latter were

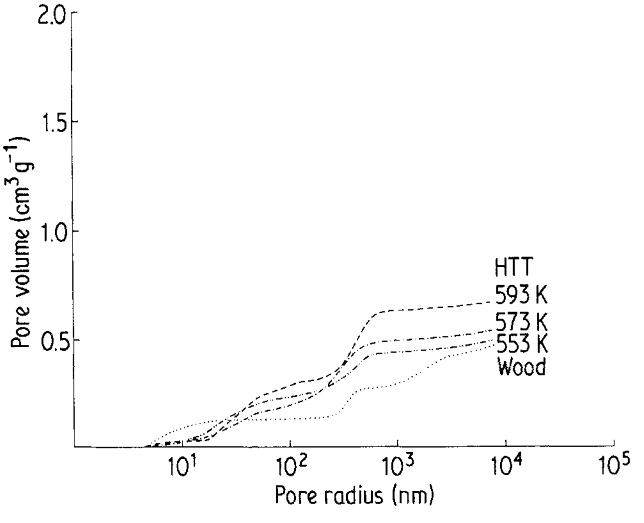


Figure 11 Variation of pore volume with pore radius, from mercury porosimetry, for charcoals prepared from Beech wood.

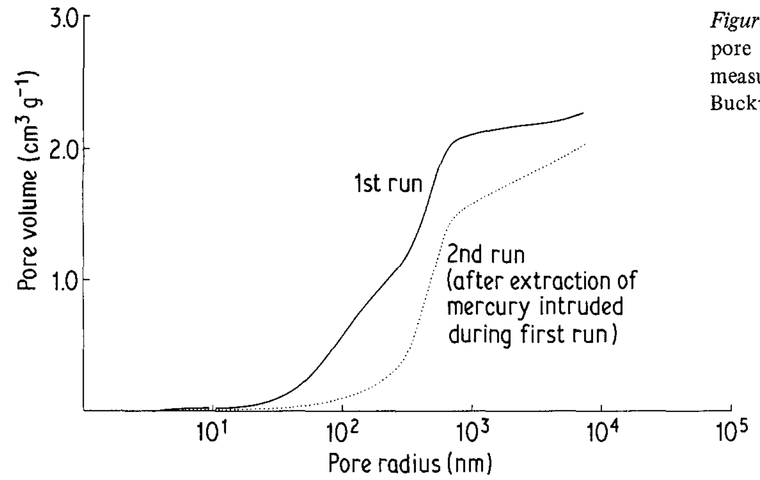


Figure 12 Variation of pore volume with pore radius, repeat mercury porosimetry measurements to assess damage, for Alder Buckthorn charcoal, HTT 573 K.

more or less spherical in shape although some of the larger particles were almost cylindrical in shape. Whereas the few larger particles showed evidence of residual structure of cell walls (approximately 10 μm in diameter), smaller particles retained little structure, at most pits of diameter less than 2 μm. None of the principal features of the parent wood were apparent and no identification of the wood was possible. The significance of the microstrength and particle shape results is, therefore, unclear. However, it seems likely that the pits observed were the openings with radius 1 μm detected by mercury porosimetry for Alder charcoal (Fig. 10).

4. Conclusions

1. Elemental analysis of charcoals has indicated that the carbonization of wood to produce charcoals for gunpowder requires extremely fine control in order to achieve the carbon contents traditionally required (70 to 80%). Thermal analysis showed that this range was achieved by partial decomposition of the cell structure of the wood and that this decomposition occurred at a lower temperature for softwood than for hardwood.

2. Decomposition of lignin and cellulose in the woods produced non-volatile products which were either chemically bonded to the resulting charcoals or else trapped in the pore structure. Such products were at maximum in charcoals produced at 573 K, corresponding to a carbon content in the charcoal of approximately 70 wt %.

3. The apparent surface areas of all the charcoals examined increased rapidly in the same temperature region in which rapid increase in carbon content occurred. Alder charcoal, HTT 373 K, appeared to have the highest surface area in this region, whereas Douglas Fir, Alder Buckthorn and Beech had surface areas similar to each other.

4. Mercury porosimetry indicated that Alder Buckthorn and Douglas Fir woods and charcoals had cumulative pore volumes greater than Alder and substantially greater than Beech charcoal. It is also indicated that the pits in charcoal extracted from gunpowder and observed by SEM may be the

TABLE X Sieve fractions in microstrength testing of charcoals prepared at 573 K

Sieve fraction	Percentage charge retained		
	Alder Buckthorn	Alder	Beech
Retained 600 μm	24	15	11
Pass 600 μm, retained 600 μm	35	36	43
Pass 212 μm	39	46	44
Lost	2	3	2

TABLE XI Particle shape analysis of charcoals prepared at 573 K

Sieve fraction		Alder Buckthorn	Alder	Beech
Retained 600 μm	Mean aspect ratio	2.2	2.4	1.7
	Range in ratios	1.0– 7.0	1.0– 7.1	1.0– 5.5
Pass 600 μm	Mean aspect ratio	2.3	2.3	1.9
Retained 212 μm	Range in ratios	1.0– 8.0	1.0– 7.0	1.0– 5.0
Pass 212 μm	Mean aspect ratio	3.3	3.6	2.5
	Range in ratios	1.0–18.5	1.0–21.3	1.0–11.0

principal sources of porosity in Alder charcoal. The structures of many of these pits are retained in charcoal contained in gunpowder.

5. Microstrength analysis showed that Beech charcoal was the most friable of the three hardwood charcoals examined.

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