Physical characteristics of baked carbons employing binary filler compositions

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A study of the characteristics of baked carbons employing different binary fillers constituted from a coarse and a fine sieve fraction of calcined petroleum coke taken in different relative proportions, has been carried out to determine the most suitable filler composition. The effect of filler composition on the properties of resulting carbons is discussed and an attempt is made to correlate the different characteristics.

1. Introduction
It is well established in the literature [1–3] that the characteristics of a carbon product depend to a large extent upon the nature of the filler, including the filler material [4] and its particle size distribution, in addition to their dependence upon the nature of the binder [5], the relative proportions of the filler and binder in the carbon mix [6, 7] and the processing conditions [8–10]. A single-sized fraction of the filler material is seldom used and, in fact, two or more fractions of different sizes are employed to constitute the filler in the actual manufacture of carbon and graphite products. The purpose of using more than one size of fractions in the filler composition is to have a good packing of particles to lead to a dense and strong carbon product of low electrical resistivity and low permeability. For reasons of simplicity and economy, however, just two fraction sizes, a coarse and a fine, can also be used to constitute the filler. However, there are few reports in the literature regarding properties of carbons made from such binary fillers. Therefore, a study of these was undertaken, and the results are reported here.

2. Experimental details
Calcined petroleum coke was used as the filler material, being the most commonly available. Sieve fractions of size (− 60 + 100) and (− 300) B.S. mesh were chosen as the coarse and fine fractions, respectively.

The calcined petroleum coke, the characteristics of which are given in Table I, was crushed, ground and sieved to obtain suitable quantities of (− 60 + 100) and (− 300) B.S. mesh fractions. The two fractions were mixed in six different relative proportions as shown in Table II and then each of these compositions, after being subjected to bulk density determination as described elsewhere [7], was dry-blended and subsequently roll-mixed at 120° C with five different proportions of a powdered coal-tar pitch, the characteristics of which are also given in Table I. The mixes obtained were hot pressed into cylindrical blocks of 20 mm diameter under a pressure of 183 kg cm⁻² at 120° C. These blocks were subjected to green-density determination and then fired in a non-oxidizing atmosphere to 950° C. Finally, the resulting baked blocks were tested for baked density, electrical resistivity, crushing strength, porosity distribution (using a mercury porosimeter up to a pressure of 1000 kg cm⁻²) and air permeability coefficient. The measurement of these characteristics was carried out as described earlier [7]. However, for permeability measurement, an apparatus based on a steady-state method was specially developed for the present investigation; this is briefly described in the Appendix and is shown in Fig. 1. The different characteristics of the various batches of baked carbons have been compiled in Tables III to VIII and summarized in Table IX.

3. Results and discussion
Table III gives the apparent densities of green carbons employing the different binary fillers with several proportions of the binder. It is observed that, in general, the optimum amount of binder corresponding to maximum green density increases as the fine

TABLE I Characteristics of filler and binder materials

Calcined petroleum coke	
Ash content	0.41%
Kerosene density	2.10 g cm⁻³
Bulk density of coarse (− 60 + 100 B.S. mesh) fraction	0.82 g cm⁻³
Bulk density of fine (− 300 B.S. mesh) fraction	0.59 g cm⁻³
Electrical resistivity of coarse fraction at a pressure of 183 kg cm⁻²	38.2 mΩ cm
Electrical resistivity of fine fraction at a pressure of 183 kg cm⁻²	45.3 mΩ cm
Coal-tar pitch	
Softening point (ring and ball)	78° C
Viscosity at 120° C	28.3 P
Density	1.30 g cm⁻³
Coking value	55%
Ash content	0.27%
Benzene insolubles	30.9%
Quinoline insolubles	12.5%
Beta-resins	18.4%

TABLE II Composition of different fillers and carbon mixes

Filler number	Proportion (wt %) of		Bulk density (g cm^{-3})	Binder content (by weight) per 100 parts of filler
	Coarse fraction	Fine fraction		
1	100	0	0.82	20, 25, 30, 35, 40
2	80	20	0.89	20, 25, 30, 35, 40
3	60	40	0.86	25, 30, 35, 40, 45
4	40	60	0.77	25, 30, 35, 40, 45
5	20	80	0.69	30, 35, 40, 45, 50
6	0	100	0.59	30, 35, 40, 45, 50

Coarse fraction = (−60 + 100) B.S. mesh.
Fine fraction = (−300) B.S. mesh.

fraction in the filler composition increases. Further, the green density at the respective optimum binder contents remains almost the same up to Filler 4 containing 60% of the fine fraction, beyond which it decreases slightly. This is reasonable since the finer fillers (5 and 6) have the higher binder demand. Such compositions, therefore, have a relatively lower green density because of the lower density of the binder pitch compared to that of the filler coke.

Table IV shows the apparent densities of baked carbons using the different binary fillers, each containing several binder contents. It is seen that the baked density obtained with the optimum binder content remains almost constant up to a fine fraction content of 60% in the filler composition (Filler 4), above which it decreases. The significantly lower baked den-

sity obtained with Filler 6 compared to the coarser fillers may be attributed to higher optimum binder demand in this case, which leads to evolution of a large amount of volatiles during baking, resulting finally in a more porous carbon product.

Table V represents the electrical resistivities of baked carbons made from the different binary fillers, each mixed with several proportions of the binder. It is observed for the different binary fillers that at the respective optimum binder contents, the electrical resistivity first decreases with increase in the fine fraction in the filler up to 60% (Filler 4), above which it starts increasing. An attempt to correlate the electrical resistivities and the corresponding baked densities obtained with the different binary fillers at the respective optimum binder contents reveals that the electrical resistivity of a baked carbon is not a function of its density alone, but may also depend on its pore structure.

Table VI shows the crushing strengths of baked carbons employing the different binary fillers, each mixed with several proportions of the binder. It is seen that for the different fillers, the crushing strength of baked carbons at the respective optimum binder contents rises with the fine fraction content up to 60% in the filler composition (Filler 4), above which it falls. A close examination of the strengths of carbons made from the different fillers at their respective optimum binder contents reveals that the crushing strength does not depend upon the porosity (estimated from the
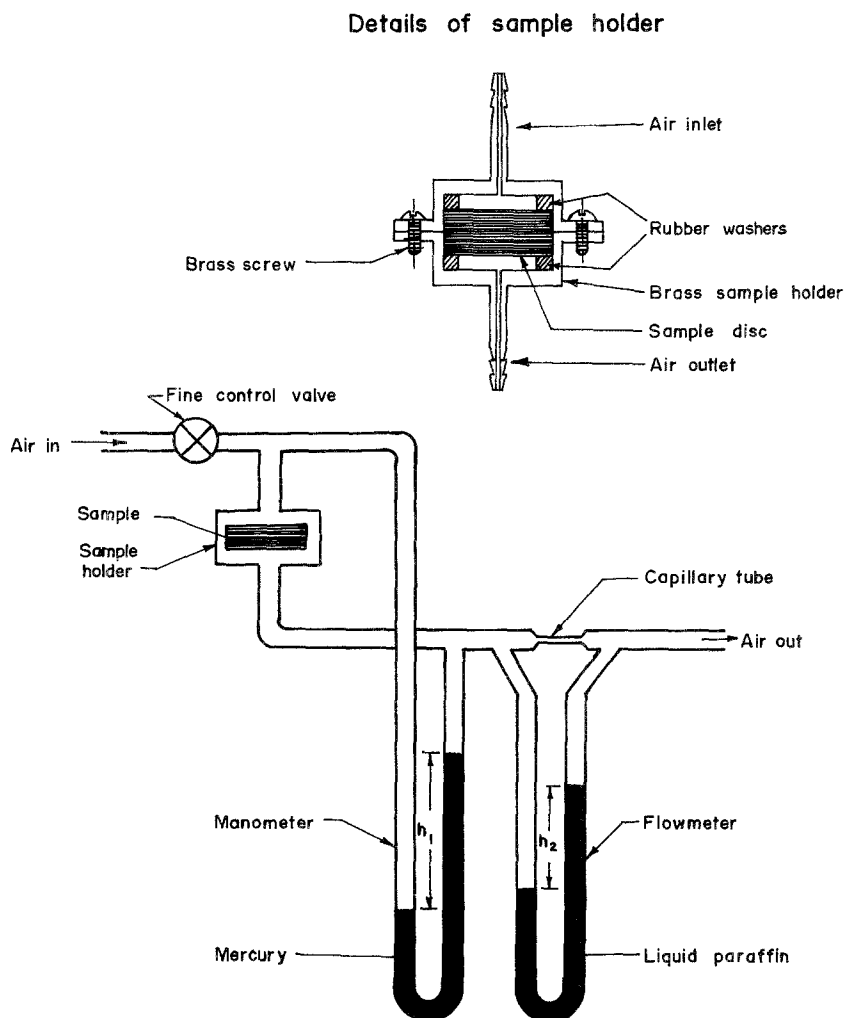
Details of sample holder

Figure 1 A schematic drawing of the apparatus for the measurement of air permeability.

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TABLE III Apparent densities of various green carbons

Filler number	Apparent densities (g cm^{-3}) of green carbons employing different fillers with binder contents of (%)							Estimated	
	20	25	30	35	40	45	50	Optimum binder content (%)	Corresponding green density (g cm^{-3})
1	1.62	1.68	1.73	1.73	1.70	–	–	30–35	1.73
2	1.62	1.68	1.72	1.72	1.69	–	–	30–35	1.72
3	–	1.68	1.72	1.71	1.69	1.67	–	30–35	1.72
4	–	1.65	1.71	1.73	1.72	1.68	–	35–40	1.73
5	–	–	1.68	1.70	1.68	1.70	1.67	35–45	1.70
6	–	–	1.63	1.66	1.68	1.68	1.69	40–50	1.69

TABLE IV Apparent densities of various baked carbons

Filler number	Apparent densities (g cm^{-3}) of baked carbons employing different fillers with binder contents of (%)							Estimated	
	20	25	30	35	40	45	50	Optimum binder content (%)	Corresponding baked density (g cm^{-3})
1	1.63	1.66	1.67	1.60	1.50	–	–	25–30	1.67
2	1.64	1.67	1.67	1.58	1.45	–	–	25–30	1.67
3	–	1.63	1.66	1.61	1.48	1.41	–	30	1.66
4	–	1.65	1.66	1.65	1.58	1.47	–	25–35	1.66
5	–	–	1.64	1.62	1.61	1.54	1.47	30	1.64
6	–	–	1.59	1.59	1.59	1.58	1.54	30–45	1.59

baked density) alone. Crack propagation in the failure of brittle solids suggests that the crushing strength of a carbon product, apart from depending (inversely) on porosity, would depend predominantly upon the size and number of relatively coarser pores (say, with diameters $\geqslant 1.5\,\mu m$), i.e. on the volume of such pores. For Fillers 1 and 4, the total pore volume or the total open porosity being more or less the same as seen in Table VII and also expected from the baked densities, the higher strength of the carbons based on Filler 4 compared to Filler 1 may, therefore, be attributed to a steep fall in the volume of relatively coarser pores (diameter $\geqslant 1.5\,\mu m$) in Filler 4-based carbons compared to those based on Filler 1. The fall in the strength of carbons made from Filler 6 compared to Filler 4 may, on the other hand, be attributed to both an increase in the total pore volume or the total open porosity besides a significant increase in the volume of relatively coarser pores.

Table VIII gives the coefficients of air permeability of baked carbons using the different binary fillers, each containing several proportions of the binder. It is obvious that the coefficient of air permeability of baked carbons first decreases with binder content to a minimum at a particular value, above which it increases. However, it is observed that the permeability coefficient exhibits a very sharp variation with binder content above the optimum value, compared to the variation below it. Thus, the coefficient of permeability is a very sensitive function of binder content in the carbon mixes when the binder exceeds the optimum quantity. This finding has great significance in those applications of carbons where the permeability is an important criterion.

A comparison of the permeability coefficients of carbons based on different binary fillers at their respective optimum binder contents (Table VIII) reveals that the permeability coefficient decreases with increasing content of fine fraction in the filler composition up to a value of 60% (Filler 4), above which it starts increasing. Comparing Fillers 1, 4 and 6 (Table VII), the fall in the permeability coefficient in case of Filler 4 compared to Filler 1 may be attributed to a steep fall in the volume of relatively coarser pores for almost the same porosity in the two cases. On the other hand, the rise in the permeability coefficient of Filler 6-based carbons over those based on Filler 4, may be due to both an increase in the total pore

TABLE V Electrical resistivities of various baked carbons

Filler number	Electrical resistivities (mΩ cm) of baked carbons employing different fillers with binder contents of (%)							Estimated	
	20	25	30	35	40	45	50	Optimum binder content (%)	Corresponding electrical resistivity (mΩ cm)
1	5.82	4.76	4.82	4.41	4.59	–	–	35	4.41
2	4.88	4.50	4.38	4.39	4.66	–	–	30–35	4.39
3	–	4.51	4.29	4.41	4.44	5.41	–	30	4.29
4	–	4.75	4.08	4.08	4.31	4.69	–	30–35	4.08
5	–	–	4.78	4.81	4.66	4.26	4.23	45–50	4.26
6	–	–	5.61	5.18	4.75	4.59	4.42	50	4.42

TABLE VI Crushing strengths of various baked carbons

Filler number	Crushing strength (N mm^{-2}) of baked carbons employing different fillers with binder contents of (%)							Estimated Optimum binder content (%)	Corresponding crushing strength (N mm^{-2})
	20	25	30	35	40	45	50		
1	60	68	64	38	30	–	–	25	68
2	54	77	78	38	20	–	–	25–30	78
3	–	71	75	48	33	18	–	30	75
4	–	69	91	87	54	26	–	30	91
5	–	–	81	80	58	49	32	30–35	81
6	–	–	70	80	76	72	57	35	80

TABLE VII Dependence of crushing strength and air permeability coefficient on porosity and its distribution in baked carbons

Filler number	Baked density (g cm^{-3})	Crushing strength (N mm^{-2})	Permeability coefficient (10^{-11} cm^2)	Volume of pores with diameter $\geq 1.5\,\mu$m (cm^3 g^{-1})	Total* pore volume (cm^3 g^{-1})	Total* open porosity (%)
1	1.67	68	1.86	0.043	0.116	19.4
4	1.66	91	0.99	0.026	0.113	18.8
6	1.59	80	2.10	0.031	0.131	20.8

*Refers to the volume of pores having diameters ≥ 15 nm (mercury intrusion pressure = 1000 kg cm^{-2}).

volume or the total open porosity along with a significant increase in the volume of relatively coarser pores.

It may be interesting to note from Table IX that the optimum binder content (OBC) with respect to crushing strength (CS) is more or less the same as that with respect to the permeability coefficient (PC). However, with respect to the other characteristics, i.e. green density (GD), baked density (BD), crushing strength (CS), and electrical resistivity (ER), the following relation, reported earlier by Bhatia and Aggarwal [4] has been found to hold:

$$(OBC)_{GD} \geqslant (OBC)_{ER} \geqslant (OBC)_{BD} \geqslant (OBC)_{CS}$$

In the face of the present finding that $(OBC)_{CS} \cong (OBC)_{PC}$, therefore, the above relation is extended to the form

$$(OBC)_{GD} \geqslant (OBC)_{ER} \geqslant (OBC)_{BD}$$

$$\geqslant (OBC)_{CS} \cong (OBC)_{PC}$$

4. Conclusions

1. A purely coarse filler (− 60 + 100 B.S. mesh) leads to a carbon product which has the highest baked density, lowest crushing strength and highest electrical resistivity together with a medium value of air permeability coefficient. On the other hand, a purely fine filler (− 300 B.S. mesh) results in a product having the lowest baked density, medium value of crushing strength, and the highest values of electrical resistivity and permeability coefficient. However, a mixture of 40 parts of the coarse fraction and 60 parts of the fine fraction leads to a carbon product having almost the highest baked density, highest crushing strength, and lowest values of electrical resistivity and coefficient of air permeability.

2. The electrical resistivity of a baked carbon is not a function of the baked density alone but may also be dependent on its pore structure.

3. The crushing strength of a carbon product, apart from depending (inversely) on the total pore volume or the total open porosity, appears to depend predominantly on the size and number of relatively coarser pores (diameter $\geqslant 1.5\,\mu$m), i.e. on the volume of such pores.

4. The coefficient of air permeability in the case of the different fillers at their respective optimum binder contents lies in a very narrow range (1 to 2 × 10^{-11} cm^2), whereas for any particular filler, it increases by orders of magnitude with increase in binder content above the optimum value. It also appears that the permeability coefficient is dependent

TABLE VIII Coefficients of air permeability of various baked carbons

Filler number	Coefficients of air permeability (10^{-11} cm^2) of baked carbons employing different fillers with binder contents of (%)					Estimated Optimum binder content (%)	Corresponding permeability coefficient (10^{-11} cm^2)
	25	30	35	40	45		
1	1.86	24.6	–	–	–	25	1.86
2	2.87	1.60	22.4	–	–	30	1.60
3	2.59	1.68	18.5	91	–	30	1.68
4	2.55	0.99	1.94	18.6	105	30	0.99
5	3.02	1.74	5.12	23.4	–	30	1.74
6	–	4.15	2.10	6.73	–	35	2.10

TABLE IX Characteristics of green and baked carbons employing different binary fillers and optimum binder contents

Filler number	Characteristics of green and baked carbons				
	Green density $(\mathrm{g\,cm^{-3}})$	Baked density $(\mathrm{g\,cm^{-3}})$	Electrical resistivity $(\mathrm{m\,\Omega\,cm})$	Crushing strength $(\mathrm{N\,mm^{-2}})$	Permeability coefficient $(10^{-11}\,\mathrm{cm^2})$
1	1.73 (30–35%)*	1.67 (25–30%)	4.41 (35%)	68 (25%)	1.86 (25%)
2	1.72 (30–35%)	1.67 (25–30%)	4.09 (30–35%)	78 (25–30%)	1.60 (30%)
3	1.72 (30–35%)	1.66 (35%)	4.29 (30%)	75 (30%)	1.68 (30%)
4	1.73 (35–40%)	1.66 (25–35%)	4.08 (30–35%)	91 (30%)	0.99 (30%)
5	1.70 (35–45%)	1.64 (30%)	4.26 (45–50%)	81 (30–35%)	1.74 (30%)
6	1.69 (40–50%)	1.59 (30–45%)	4.42 (50%)	80 (35%)	2.10 (35%)

*Figures in parentheses denote the optimum binder contents.

on both the total pore volume and the volume of relatively coarser pores.

5. The optimum binder content, with respect to crushing strength is more or less the same as that with respect to the permeability coefficient. Therefore, the old relation correlating the optimum binder contents with the different characteristics under study is extended to a new form:

$$(\mathrm{OBC})_{\mathrm{GD}} \geqslant (\mathrm{OBC})_{\mathrm{ER}} \geqslant (\mathrm{OBC})_{\mathrm{BD}}$$
$$\geqslant (\mathrm{OBC})_{\mathrm{CS}} \cong (\mathrm{OBC})_{\mathrm{PC}}$$

Acknowledgements

Appendix

The principle underlying the measurement of air permeability coefficient is to pass air through the cross-section of a sample disc (cut from cylindrical blocks) mounted in a special brass-holder and measure its flow rate through the other end under steady-state conditions, by a capillary flowmeter connected in series with the sample disc. The sides (cylindrical surfaces) of the discs were, however, coated with a thermosetting resin (Araldite) to prevent any flow of air through them. The pressure drops across the sample $(h_1 \varrho_1 g)$ and across the flowmeter capillary $(h_2 \varrho_2 g)$ were measured on differential manometers containing suitable liquids (mercury and liquid paraffin, respectively), and adjusted to be such that compressibility of air and slip flow, if any, could be neglected. Under these conditions, in the steady-state, using the Darcy's and Poseuille's equations, the expression for the air permeability coefficient (K) could be easily derived as

$$K = C \frac{h_2}{h_1} \frac{t}{A}$$

where $C = \pi r^4 \varrho_2 / 8 l \varrho_1$ (a constant of the apparatus), and h_1 and h_2 are heights of the mercury and liquid paraffin, respectively, in the differential manometers; ϱ_1 and ϱ_2 the densities of mercury and liquid paraffin, respectively; t the thickness of the sample disc; A the area of cross-section of the sample disc; r the radius of the capillary; l the length of the capillary.

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