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A comparative study of the characteristics of baked carbon mixes employing different filler materials

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A study of the physical characteristics of baked carbon mixes employing calcined petroleum coke, coal-tar pitch coke, metallurgical coke and anthracite coal has been made to explore their relative suitability and area of application. It is revealed that petroleum coke and pitch coke lead to a carbon product of almost the same density and electrical resistivity. However, the crushing strength of the product employing pitch coke is $1\frac{1}{2}$ times that of the one employing petroleum coke. The carbon product produced from the metallurgical coke is found to be slightly inferior in respect of density and electrical resistivity and slightly superior in respect of crushing strength when compared with that made from petroleum coke. The use of anthracite coal results in a carbon product of significantly lower density and much higher electrical resistivity than that of the product using the petroleum coke. However, the strength of the anthracite coal-based carbons is found to be nearly double that of the petroleum coke-based carbons. Thus, the significance of the present study lies in the fact that the above findings help one to estimate a possible filler composition for a carbon product possessing the desirable critical characteristics.

1. Introduction

Carbon products are fabricated mainly from a mixture of carbonaceous filler such as petroleum coke, pitch coke, metallurgical coke, etc., and a carbonaceous binder, e.g. coal tar pitch. The mixture, after being shaped by compression moulding or extrusion into an artefact of the desired shape and size, is fired in a non-oxidizing atmosphere to produce a rigid carbon product, the properties of which depend on the nature of the filler and the binder, their relative proportions and the processing conditions. A search of the literature reveals that many investigations have been reported on the physical characteristics of carbon mixes employing petroleum coke as the filler (e.g. [1–8]). The latter is used because of its high density, low electrical resistivity and coefficient of thermal expansion, low ash and sulphur contents together with high graphitizability. Other filler materials such as coal-tar pitch coke, metallurgical coke, anthracite coal, etc., have also been used in certain specific areas of application of the manufactured carbon. However, no systematic and comparative data are available concerning the use and the relative characteristics of the baked carbons obtained from the above filler materials. Further, it is well known that the crude oil source has a profound effect on the nature of the resultant petroleum coke. In general, impurities of metals and heteroatoms (such as sulphur, nitrogen and oxygen) relate closely to impurities in coke made from these crudes [9]. These impurities, in turn, are likely to affect the physical characteristics and performance of the artificial carbon and graphite. Furthermore, it is believed that cokes available during the next decade will either have higher contents of impurities because they will

TABLE I Characteristics of the different filler materials

No.	Filler	Sieve analysis of filler (B. S. mesh)	Volatile matter content (%)	Ash content (%)	Bulk density ($g\,cm^{-3}$)	Kerosene density ($g\,cm^{-3}$)	Electrical resistivity at 200 $kg\,cm^{-2}$ ($m\,\Omega\,cm$)
1	Calcined petroleum coke	(– 300)	Nil	0.96	0.61	2.10	52
2	Coal-tar pitch coke	(– 300)	Nil	3.17	0.57	2.03	39
3	Metallurgical coke	(– 300)	2.9	6.26	0.66	1.97	96
4	Anthracite coal	(– 300)	8.0	12.89	0.50 0.58*	1.83 1.93*	442×10^3 275*

*Refers to the calcined (1000° C) anthracite coal.

come from residues that present a disposal problem, or be more expensive if they are produced intentionally rather than as a by-product. Efforts are, therefore, now being made to replace calcined petroleum coke with relatively cheaper materials such as metallurgical coke, coal-tar pitch coke and anthracite coal in the manufacture of a number of carbon products. In the light of the above observations, an attempt was made to study systematically the physical characteristics of baked carbon mixes, employing different filler materials. The present paper is the result of such an attempt.

2. Experimental procedure

The different filler materials used in the present study consisted of calcined petroleum coke, coal-tar pitch coke, metallurgical coke and anthracite coal, the specifications of which are given in Table I. The above filler materials were subjected to bulk density measurements described elsewhere [7, 10] and powder resistivity measurements prior to their wet mixing. The apparatus for measuring the powder resistivity of the above filler materials consisted of a vertical thick-walled perspex cylinder, of i.d. 20 mm, resting on a thick brass plate into which a thick brass plate piston moved freely. The powdered fillers were taken into the perspex cylinder and compressed to about 19.6 MPa in a compression machine. Care was taken that no powder was wedged between the walls of the piston and the perspex cylinder, since the friction created decreases the real pressure exerted on the powder and thus invalidates the results. The electrical resistivity was measured by passing a suitable current through the powdered filler bed of known length, and recording the potential drop at its two ends with help of a precision microvoltmeter.

TABLE II Characteristics of coal-tar pitch binder

1	Softening point (R&B)	= 78° C
2	Density	= 1.24 $g\,cm^{-3}$
3	Coking value (Conradson)	= 58%
4	Ash content	= 0.29%
5	Benzene insolubles	= 38%
6	Quinoline insolubles	= 12.4%
7	Carbon content	= 94.7%
8	Hydrogen content	= 3.60%
9	Nitrogen content	= 1.13%
10	Sulphur content	< 0.5%
11	Aromaticity (C/H atomic ratio)	= 2.19

100 g portions from each of the filler materials were then wet mixed with varying proportions of a medium hard coal-tar pitch binder having the characteristics given in Table II and then roll mixed for 15 min each at a temperature of 120° C. The carbon mixes so obtained were ground cold to pass through a 60 B.S. mesh. About 12 g portions from each of these powdered mixes were moulded into cylindrical blocks of about 19 mm diameter under a pressure of 19.6 MPa at a temperature of 120° C. These blocks were then measured for the green density determination and subsequently baked in an electrical muffle furnace to a temperature of 950° C in a 5-day baking cycle. The baked blocks were finally subjected to apparent density, electrical resistivity and crushing strength measurements as described previously [7]. The data of these measurements are plotted in Figs. 1 to 4 and the results obtained have been summarized in Table III.

3. Results and discussion

Figs. 1 and 2 represent, respectively, the variation

TABLE III Comparative data of the characteristics of green and baked carbon mixes employing different fillers and optimum contents of coal-tar pitch binder

No.	Filler	Characteristics of green and baked carbon mixes				
		Green density ($g\,cm^{-3}$)	Baked density ($g\,cm^{-3}$)	Crushing strength ($N\,mm^{-2}$)	Electrical resistivity ($m\,\Omega\,cm$)	Volume shrinkage (%)
1	Calcined petroleum coke	1.69 (45–50%)	1.62 (45%)	59 (40%)	2.97 (45–50%)	6.3
2	Coal-tar pitch coke	1.69 (48–52%)	1.63 (50%)	92 (50%)	2.67 (50%)	6.6
3	Metallurgical coke	1.67 (45–50%)	1.60 (45%)	68 (41–43%)	4.08 (45–50%)	5.4
4	Anthracite coal	1.53 (45%)	1.56 (44%)	113 (43%)	6.40 (45%)	13.5

Note: Figures in parentheses denote optimum binder content.

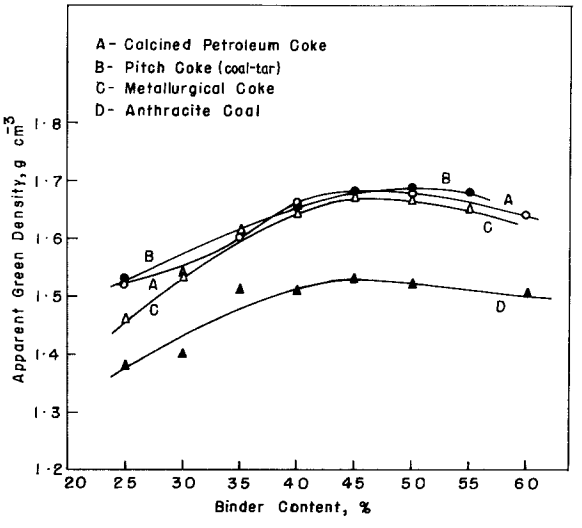

Figure 1 Variation of apparent densities of green carbon mixes employing different fillers with various proportions of binder.

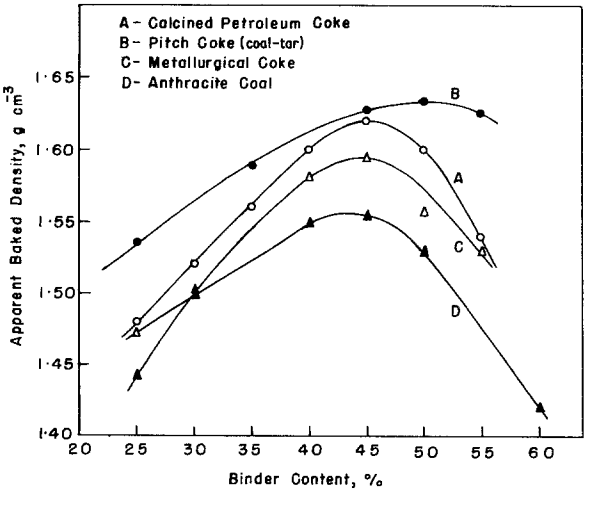

Figure 2 Variation of apparent densities of baked carbon mixes employing different fillers with various proportions of binder.

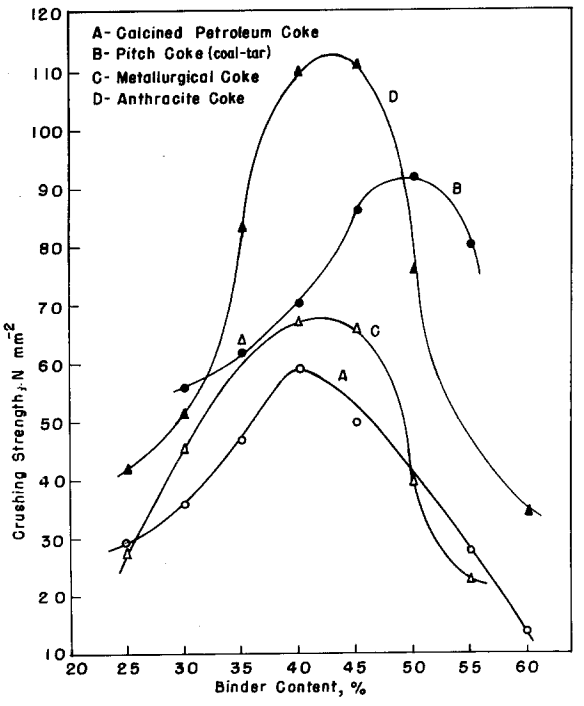

Figure 3 Variation of crushing strengths of baked carbon mixes employing different fillers with various proportions of binder.

of apparent densities of green and baked carbon mixes with the increase in binder content corresponding to various filler materials. As is obvious, the apparent density of green or baked carbon mixes increases with the increasing binder content up to a certain level, above which it begins to decrease. The density of the baked carbon mixes employing petroleum coke or coal-tar pitch coke is found to be almost the same and the highest, while that of the mix employing anthracite coal gave the lowest value of all the filler materials used. The maximum values of the density of the baked carbons made using a particular filler material may, however, be qualitatively correlated to the kerosene density.

Fig. 3 shows the variation of crushing strength of baked carbon mixes for different fillers with increasing proportions of binder. As is the case with green or baked density considerations, regardless of the nature of the filler, the crushing strength of baked carbon mixes continues to increase with the increasing binder content upto a certain limit, above which it begins to fall. It is seen, however, that out of all filler materials, the anthracite coal leads to the strongest carbon possessing a strength of 113 N mm^{-2}, a value which is nearly double that obtained using calcined petroleum coke. Furthermore, the coal-tar pitch coke results in a carbon having a strength of about $1\frac{1}{2}$ times that of the one employing petroleum coke. It is also observed that in the case of anthracite coal, there is a steep rise or fall in the strength of the carbons with variation in the binder content around the optimum. The high strength of the anthracite coal-based carbon may be explained by the hypothesis that when the corresponding green carbon is baked, the volatiles given off by the filler particles create openings thereby giving a relatively better opportunity to the binder to enter the filler particles and resulting in the formation of stronger binder–coke bonds leading finally to a stronger carbon product. However, the above hypothesis may be limited to a certain level of volatile matter in the filler material.

Fig. 4 represents the variation of electrical resistivity of different filler-based carbon mixes with increasing proportion of binder. As is expected, the electrical resistivity of the baked carbons continues to decrease with increasing binder content upto a certain level above which it starts increasing. It is clear from the figure that the pitch coke-based carbons have a lower electrical resistivity than the petroleum coke-based ones, which suggests that the pitch coke is an equally suitable filler material as the petroleum coke. The electrical resitivity of metallurgical coke-based carbon is about 4 m Ω cm and is higher than that

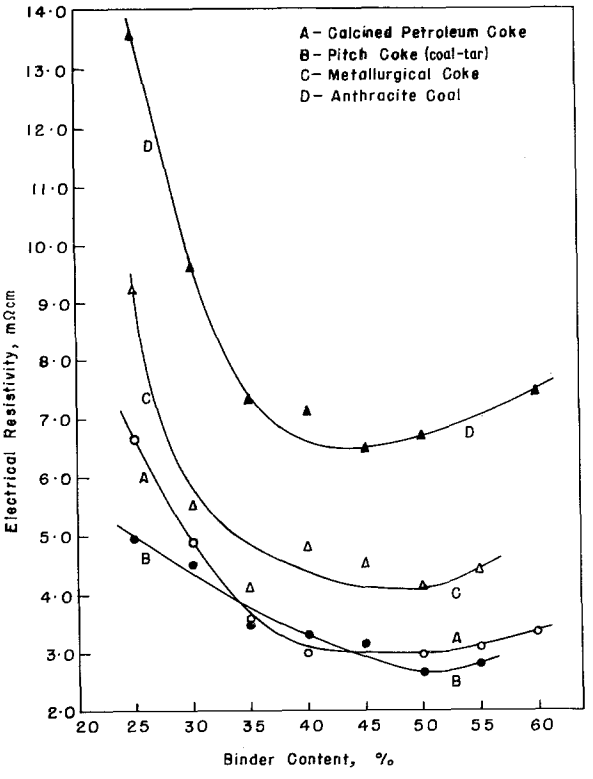

Figure 4 Variation of electrical resistivities of baked carbon mixes employing different fillers with various proportions of binder.

obtained from either coal-tar pitch coke or petroleum coke but is still suitable for applications of carbon products where a resistivity value as high as 6 m Ω cm may be tolerated. However, the electrical resistivity of the anthracite coal-based carbon is the highest and has a value of 6.4 m Ω cm at the optimum binder level. This is consistent with the inherent high value of its resistivity in the powder form compared to that of the other filler materials.

It is interesting to note from Table III that the petroleum coke and coal-tar pitch coke fillers lead to a carbon product having almost the same density and electrical resistivity, while the crushing strength of the latter is higher than that of the former. This shows that pitch coke may be a possible alternative to petroleum coke for many applications of baked carbons. The significance of Table III lies in the fact that depending upon the critical properties desired of a carbon product, one can choose and formulate the required filler composition. Further, it is observed from the figures given in parentheses denoting the optimum binder content, that the optimum binder content in a carbon mix varies with the physical characteristics of the carbon product. This seems to be true of every filler. However, a close examination shows that the optimum binder contents required from the view point of different characteristics in a carbon product, satisfy the following relation regardless of the nature of filler:

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

where, OBC is the optimum binder content, GD the green density, ER the electrical resistivity, BD the baked density, and CS the crusing strength. Thus one has to formulate a critical filler composition and make a compromise in selecting the optimum binder content with respect to the properties desired of the final carbon product.

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