

GAS REACTIVITY OF CARBONS PRODUCED FROM COAL TAR PITCHES

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SOMMAIRE

Vingt-cinq échantillons de brai de houille, obtenus à partir de goudrons des fours à coke à température élevée, ont été carbonisés, cokésifiés et graphités dans des conditions déterminées. On a mesuré les réactivités de tous ces coques et carbones graphités avec le gaz carbonique à 1150 °C on a mesuré aussi les réactivités de la plupart des échantillons avec l'air à 700 °C. On a étudié, sur des échantillons sélectionnés, l'influence des variations de la température de graphitisation et du chauffage en atmosphère chlorée sur la réactivité ultérieure avec le gaz carbonique et l'air. Pour des coques et carbones graphités sélectionnés on présente les résultats obtenus en ce qui concerne les surfaces spécifiques et les paramètres cristallographiques. Les résistivités électriques ont été déterminées pour tous les échantillons.

A quelques exceptions près, les carbones graphités ont une réactivité considérablement plus élevée vis-à-vis du gaz carbonique que les coques correspondants. Les résultats sont inversés pour la réactivité des échantillons vis-à-vis de l'air. La variation de la température de graphitisation a une influence très marquée sur la réactivité ultérieure des carbones vis-à-vis du gaz carbonique. On discute des explications possibles des résultats obtenus pour les réactivités.

Introduction.

Coal tar pitch, derived from by-product ovens, is the preferred material for use as a binder in the manufacture of carbon and graphite electrodes. Variations in the type of coke oven and coke oven practice and the diversity of sources of supply give rise to variations in pitch quality which affect electrode performance and result, in the case of some pitch binders, in poor performance. At the moment, it seems in vogue for industry to invariably blame poor electrode performance on the binder, despite variations in the properties of the filler (usually petroleum coke), which may be as great as those variations in binder properties. It appears that the main justification for attributing poor electrode performance to the binder is the feeling that coal tar pitch coke does not grow in crystallite size as markedly as does petroleum coke upon heat treatment. With the attendant smaller growth in crystallite size, it is suggested that the pitch

binders possess inferior quality for such important properties as reactivity to oxidizing gases, electrical and thermal conductivity, coefficient of thermal expansion, and strength.

The three initial aims of this research have been: (1) to seek relationships between the chemical and physical properties of coal tar pitches and the properties of the coques and graphitized carbons produced therefrom; (2) to better understand the effect of heat treatment temperature and atmosphere on the properties of carbons produced from coal tar pitch; and (3) to compare the properties of the coques and graphitized carbons produced from coal tar pitch with those produced from a standard, commercially used petroleum coke. In particular, the reactivity of the coques and graphitized carbons to CO₂ and air is of interest.

Experimental.

A. Preparation of Cokes and Graphitized Carbons.

1. *Charring of the coal tar pitches.* — A sample of 250 g of coal tar pitch was placed in an annealed glass liner (5,4 cm o.d. and 52,5 cm long). The liner was enclosed in a gas-tight steel bomb (1 780 cm³ capacity), and the bomb was evacuated prior to filling with N₂ to atmospheric pressure. The bomb was heated to 550 ± 2,5 °C in twelve hours and held at 550 °C for an additional twelve hours. The maximum pressure developed on charring ranged from 710 to 890 psig., depending upon the pitch. The bomb was allowed to cool to room temperature before opening.

The recovery of char inside the glass liner, which was subsequently coked and graphitized, generally ranged from 67 to 78 % of the initial pitch weight. The remainder of the weight could be accounted for by char between the glass liner and bomb wall and by permanent gases. The molecular weight of the permanent gases was estimated in several runs

to be about 22. Two charring runs were made on each pitch, with the charring yields agreeing consistently within 1,5 %.

2. *Grinding of the coal tar pitch chars.* — The pitch-chars were ground in a hammer mill and screened through U.S. sieves 40 and 60 mesh. The 40 × 60 mesh fraction, which amounted to between 30 and 40 % of the char yield, was used in the subsequent coking operation.

3. *Coking of the coal tar pitch chars.* — Twenty-five g of char from each charring run were heated (in a Vycor tube flushed with He) at a rate of 5 °C per minute to 1 000 °C and soaked for one hour at this temperature. Variation in temperature along the sample length was less than ± 6 °C. The coke yield amounted to about 65 to 70 % of the initial pitch weight. Negligible fusing of the 40 × 60 mesh char particles was found on coking.

4. *Graphitization of the coal tar pitch cokes.* — Approximately 10 g of 40 × 60 mesh coke were placed in cylindrical graphite capsules (1 1/2 in o.d. and 1 1/2 in long). The capsules were loaded into a larger cylindrical graphite capsule (4 in o.d. by 11 in long), which was then centered in a resistance furnace. The resistance furnace, which was flushed with He during a run, consisted of a graphite tube 6 in in diameter and several ft long. Samples were allowed to cool to room temperature before being removed. All temperatures were measured with a Pyro optical pyrometer.

5. *Additional heat treatment of a variety of carbons.* — In order to understand the effects of a wide heat treatment range on the subsequent reactivity of coal tar pitch coke and petroleum coke to oxidizing gases, samples were heated to temperatures of approximately 1 750, 2 000, 2 250, 2 600 and 2 800 °C in an induction furnace, with zero soak time at the maximum temperature. Three cylindrical graphite crucibles (7/8 in o.d. and 1 1/2 in long) were partially filled with 5 g of sample. The crucibles were inserted into a graphite tube (1 1/4 in o.d. and 21 in long). The furnace was evacuated over night at room temperature and then flushed either with He or with a 1 % Cl₂ — 99 % He mixture during the run. The temperature was regulated by manual control of a transformer. Temperature readings were taken with an optical pyrometer sighted through a quartz window at the top of the furnace.

B. Apparatus and Procedures Used to Define the Properties of the Pitches, Cokes, and Graphitized Carbons.

1. *X-Ray diffraction studies.* — A 164° (2 θ) General Electric x-ray diffraction unit XRD-3, emitting a

radiation filtered through a Ni foil was used to determine crystallographic data on the cokes and graphitized carbons. The procedures employed in determining crystallite sizes, interlayer spacings, and crystallite orientation have been thoroughly described (¹).

2. *Surface area studies.* — Specific surface areas of some selected chars, cokes, and graphitized carbons were determined from adsorption isotherms of N₂ at 77 °K using the BET equation (^{2, 3}). Equilibrium was reached quickly for all adsorption points on all samples studied.

3. *Electrical resistivity studies.* — Electrical resistivities were determined on 40 × 60 mesh samples of all cokes and graphitized carbons. A 2 g sample was held in a steatite container (1/2 in o.d. and 2 in long). Known pressures were applied to the sample through steel, copper tipped plungers using a standard laboratory hydraulic press. A detailed description of the experimental procedure used is found elsewhere (⁴).

4. *Reactivity studies.* — Reactivities of 2 g samples of 40 × 60 mesh material in CO₂ at 1 150 °C and air at 700 °C were determined in a particle reactor previously described by WALKER and NICHOLS (⁵). Reactivities were expressed as per cent of sample reacting over a 2 hour period. Procedures employed were also similar to those previously described (⁵).

5. *Chemical analyses and miscellaneous properties of the coal tar pitches.* — Analyses of the coal tar pitches were determined using standard specification tests (⁶).

C. Description of Raw Materials.

The coal tar pitches represent the residual product from the distillation of high temperature coke-oven tars. No information is available on the carbonization temperatures at which the tars were produced or the distillation procedures used to produce the coal tar pitches.

Raw petroleum coke is the coked still bottoms left in the pot after distillation of the crude oil. The raw coke having seen a temperature of ca 500 °C was calcined at ca 1 250 °C. It had an ash content of 0,12 % and a carbon content of 97,8 %.

Results.

A. Analyses of the Coal Tar Pitches.

Table I presents data on the chemical analyses of the whole pitches. The analysis for sample BD-PSU-5 is markedly different from the remaining samples,

TABLE I
Chemical analyses of the pitches.

Pitch	% C	% H	% N	% S	% Other (*)	% Ash	Atomic C — H Ratio
22 761	93,32	4,20	0,75	0,75	0,98	0,10	1,86
22 763	93,43	4,24	0,68	0,52	1,13	0,09	1,85
22 805	92,43	4,31	0,88	0,41	1,97	0,24	1,80
23 217	92,05	4,52	0,50	0,54	2,39	0,13	1,71
56-273	93,39	4,31	0,92	0,60	0,78	0,08	1,82
56-274	92,95	4,49	0,86	0,35	1,35	0,15	1,74
BD-PSU-1	93,35	4,32	1,08	0,27	0,98	0,17	1,81
-2	91,70	4,55	1,31	0,53	1,91	0,63	1,69
-3	92,77	4,32	1,21	0,58	1,12	0,07	1,80
-4	93,34	4,10	1,10	0,49	0,97	0,05	1,91
-5	81,67	7,31	1,16	0,77	9,09	2,55	0,94
-6	93,34	4,38	1,01	0,30	0,97	0,12	1,79
-7	93,36	4,44	1,00	0,31	0,89	0,14	1,77
-8	93,26	4,40	1,01	0,24	1,09	0,11	1,78
-9	93,18	4,46	1,00	0,32	1,04	0,10	1,76
-10	93,47	4,44	0,98	0,25	0,86	0,05	1,77
-11	93,25	4,49	0,99	0,31	0,96	0,05	1,74
-12	93,31	4,46	1,01	0,31	0,91	0,04	1,76
-13	93,17	4,57	1,00	0,30	0,96	0,03	1,71
-14	93,00	4,20	1,06	0,41	1,33	0,25	1,86
-15	93,08	4,29	1,06	0,47	1,10	0,22	1,82
-16	92,24	4,53	1,11	0,39	1,03	0,06	1,72
-17	92,78	4,65	1,10	0,37	1,10	0,06	1,68
-18	93,13	4,42	1,08	0,37	1,00	0,08	1,77
-19	93,13	4,49	1,11	0,37	0,90	0,08	1,74

(*) Includes % Ash.

since it is a lignite pitch. Table II presents semi-quantitative data on the concentration of metallic impurities in some selected pitches.

temperature for seven minutes. As pointed out by MARTIN and NELSON (?), this test gives a coking value considerably below that found commercially

TABLE II
Concentration of metallic impurities in selected pitches.
Concentration, PPM.

Pitch	Al	B	Ca	Cu	Fe	Mg	Mn	Na	Ni	Pb	Si	Ti
22 761	7,4	—	8,4	2,0	128	2,2	2,8	98	—	23	41	—
22 763	6,9	—	3,5	4,5	44	2,2	1,6	40	—	22	17	—
22 805	72	—	99	19	98	9,6	4,3	206	—	53	96	—
23 217	22	—	9,6	1,8	46	5,2	2,3	220	—	23	43	—
56-273	17	—	25	1,3	35	4,2	2,5	31	—	19	72	—
56-274	36	—	22	7,3	116	12	9,3	78	—	69	48	—
BD-PSU-2	310	0,88	110	5,0	360	23	11	—	21	11	510	25
-4	12	0,14	6,4	1,3	58	2,0	1,2	—	2,8	8,5	120	1,4
-5	2 400	67	160	15	1 200	180	160	—	33	72	3 100	260
-6	100	0,14	46	1,6	96	6,4	7,4	46	4,5	34	130	7,4
-9	97	0,085	23	0,92	79	6,7	4,4	28	3,0	58	120	9,4
-11	28	0,019	13	0,63	43	1,6	1,7	37	1,8	26	27	2,3
-12	27	0,020	17	0,90	40	2,8	4,6	42	3,5	35	60	6,0
-13	59	0,031	52	1,1	90	3,9	9,8	90	6,1	59	57	6,2
-14	170	0,12	75	2,9	180	16	13	57	4,2	68	360	16
-16	24	0,0062	23	0,48	86	3,4	5,8	39	1,8	56	22	1,0
-18	28	0,016	13	0,62	98	3,4	5,2	32	2,0	41	43	1,9
-19	62	0,028	120	0,80	150	7,0	8,5	50	2,9	60	100	4,3

Table III presents miscellaneous data on the pitches. The coking values were determined using the BARRETT Method B-8 (°), which consists of rapidly heating the pitch to 900 °C and holding the

upon the baking of green electrodes. The test, however, does give a relative indication of the coking value of the binder pitch. The softening point of the pitches was determined by the ring and ball method (°).

TABLE III
Miscellaneous properties of the pitches

Pitch	Coking Value	Sp. Gr., 25 °C	Soft. Pt., °C	% Insoluble in	
				Quinoline	Benzene
22 761	44,5	1,328	95,5	14,9	32,1
22 763	43,8	1,333	98,0	16,5	36,4
22 805	41,0	1,315	95,0	12,8	27,1
23 217	44,2	1,292	96,0	7,8	25,2
56-273	43,0	1,320	95,0	13,9	33,2
56-274	39,2	1,305	99,9	7,8	32,0
BD-PSU-1	42,8	1,318	94,6	15,8	32,5
-2	35,7	1,298	100,0	5,7	25,5
-3	40,0	1,318	96,0	13,3	27,1
-4	41,7	1,340	101,8	13,4	27,8
-5	24,8	1,174	103,0	8,6	18,9
-6	41,5	1,313	95,2	13,0	29,4
-7	39,8	1,306	88,7	12,2	28,4
-8	37,5	1,307	94,5	10,2	22,5
-9	36,2	1,300	89,5	9,9	20,2
-10	40,5	1,308	94,7	11,6	28,3
-11	37,1	1,297	87,0	3,8	23,7
-12	36,1	1,299	95,0	7,6	19,6
-13	33,3	1,292	88,5	6,0	17,9
-14	42,3	1,328	96,5	18,1	28,6
-15	40,2	1,314	88,2	17,2	27,2
-16	34,7	1,294	97,0	5,2	17,5
-17	32,3	1,286	85,5	5,1	16,3
-18	40,1	1,306	99,0	10,4	25,9
-19	36,1	1,296	87,5	8,3	24,2

B. Chemical Analyses of the Cokes
from the Group A (*) Coal Tar Pitches.

Table IV presents data on the chemical analyses of the cokes from the Group A coal tar pitches. For these pitches, two charring runs and three coking runs were made, with the char from one run being coked twice. The data, consequently, represent an average of three coking runs.

TABLE IV
Chemical analyses of the cokes from the group a coal tar pitches

Coke	% C	% H	% N	% S	% Other	Atomic C — H Ratio
22 761	98,16	0,48	0,23	0,54	0,57	17,2
22 763	97,68	0,61	0,03	0,35	0,35	13,4
22 805	96,53	0,79	0,16	0,26	0,26	10,6
23 217	97,96	0,44	0,36	0,26	0,26	18,5
56-273	98,35	0,56	0,00	0,29	0,29	14,1
56-274	98,11	0,75	0,05	0,16	0,16	11,4

C. Crystallographic Parameters for the Chars,
Cokes, and Graphitized Carbons from the Group
A Coal Tar Pitches.

1. Interlayer spacings and crystallite heights. — Table V presents data on the interlayer spacings and

(*) The first six coal tar pitches, on which some additional work was done, will be called Group A pitches hereafter. The remainder of the pitches will be called Group B.

crystallite heights of the chars, cokes, and graphitized carbons produced from the Group A coal tar pitches. X-ray diffraction determinations were made on a sample from each run. Consequently, the data on the chars represent the average of two determinations; on the cokes, an average of three determinations; and on the graphitized carbons, an average of two determinations at each temperature (that is, two different samples of coke were heated in each

graphitization run). The graphitization runs were performed in the resistance furnace previously described. The interlayer spacing data in all cases are significant to $\pm 0,02$ Å, $\pm 0,01$ Å, and $\pm 0,01$ Å. for the chars, cokes, and graphitized carbons, respectively. The crystallite height data in all cases are significant to ± 1 Å, ± 1 Å and ± 50 Å, respectively. The difficulty in accurately determining crystallite sizes above 500 Å from x-ray diffraction line broadening is well understood (*).

FRANKLIN⁽⁸⁾ and BACON⁽⁹⁾ have thoroughly discussed the use of interlayer spacing data as a criterion of three-dimensional ordering in carbon. Interlayer spacings above 3,44 Å are indicative of only two-dimensional ordering, whereas decreasing spacings between 3,44 Å and 3,3538 Å indicate a progressive increase in three-dimensional ordering between zero and 100%. As expected, the interlayer spacing data on the chars and cokes indicate no three dimensional ordering. Furthermore, for each group the spacings are essentially the same. In line with the findings of KINNEY, NUNN and WALKER⁽¹⁰⁾, among others, the interlayer spacings of the material having seen 1 000 °C (cokes) are somewhat larger than the comparable material having seen only 550 °C (chars). As expected, the calcined petroleum coke having seen a temperature of ca 1 250 °C has a lower interlayer spacing than the cokes from the coal tar pitches. That is, the interlayer spacing of carbons begins to decrease markedly at heat treatment temperatures above 1 050 °C.

On graphitization, a marked decrease in interlayer spacing of all the cokes is seen. The effect of increasing graphitization temperature on further decreasing the interlayer spacing is also evident, as previously discussed⁽¹¹⁾. The carbon produced from pitch 23 217 by graphitization at 2 650 °C is seen to have the lowest interlayer spacing, 3 359 Å, and, consequently, the highest degree of three-dimensional ordering, ca 85%. The petroleum coke graphitized at 2 570 °C has a lower interlayer spacing than the

height than any of the pitch cokes, as expected because of its higher calcination temperature. Extensive increases in average crystallite heights of the pitch cokes on graphitization are noted. However, the effect of increasing the graphitization temperature from 2 570 to 2 650 °C on increasing the crystallite heights is not indicated clearly by the data. In any event, the marked decrease in interlayer spacing and increase in crystallite height upon heating to graphitization temperatures clearly stamp these pitch cokes as «graphitizable carbons».

D. Surface Areas of the Chars, Cokes, and Graphitized Carbons from the Group A Coal Tar Pitches.

Surface areas were determined for at least two basic reasons. First, it was desired to compare the surface areas of the cokes and graphitized carbons with their reactivity to CO₂ and air. In much previous work on conventional electrode bodies^(5, 12, 13), however, no systematic correlation has been found between reactivity and area. Second, it has been shown for carbon blacks of large and widely different surface areas that the larger the area, the less the increase in crystallite size and decrease in interlayer spacing upon graphitization⁽¹⁴⁾. It was desired to check the possible existence of such a correlation in the present work.

TABLE V
Interlayer spacings and crystallite heights of the chars, cokes, and graphitized carbons produced from the group a coal tar pitches.

Sample	Interlayer Spacing, Å.				Crystallite Height, Å.			
	Char	Coke	Graphitized Carbon		Char	Coke	Graphitized Carbon	
			2 570 °C	2 650 °C			2 570 °C	2 650 °C
—	—	—	—	—	—	—	—	—
22 761	3,54	3,58	3,370	3,363	18	14	618	613
22 763	3,56	3,57	3,367	3,362	16	15	686	710
22 805	3,55	3,57	3,369	3,364	17	14	653	702
23 217	3,52	3,55	3,365	3,359	19	15	734	895
56-273	3,53	3,56	3,367	3,363	17	15	(789)	720
56-274	3,53	3,56	3,365	3,362	19	14	738	904
petroleum coke	—	3,51	3,364	—	—	25	—	—

majority of the pitch cokes graphitized at the same temperature. Unfortunately, the petroleum coke was not heat treated at 2 650 °C.

From Table V, it is seen that there is little significant difference in the average crystallite heights between the chars, as a group, or between the cokes, as a group. Some decrease in the average crystallite sizes of the cokes over the comparable chars are noted, in line with previous findings⁽¹¹⁾. The petroleum coke has a considerably higher crystallite

Table VI presents surface area data on 40 × 60 mesh samples of coke and graphitized carbons produced from the Group A coal tar pitches. The surface area for the char produced from pitch 23 217 is also included. Determinations were made on the same number of samples as in the x-ray diffraction studies, with the average surface areas reported in Table VI representing all samples from a given pitch within at least ± 10%.

The first major conclusion to be drawn from the

data in Table VI is that the surface areas of the cokes (and char) are quite small. These small areas indicate that the cokes (and char) contain a negligible amount of porosity in fine pores. It should be noted that the petroleum coke has a somewhat higher area than the coal tar pitch cokes. This could be due entirely, or in part, to the higher heat treatment temperature of the petroleum coke, since it has been shown that surface areas of some carbons do increase slightly when heated in the range 950 to 1 100 °C.

TABLE VI

Surface areas of the chars, cokes, and graphitized carbons
Produced from the group a coal tar pitches.

Sample	Char	Surface Area, m ² /g		
		Coke	Graphitized Carbon	
			2 570 °C	2 650 °C
22 761	—	0,36	0,18	0,18
22 763	—	0,24	0,17	0,21
22 805	—	0,26	0,17	0,20
23 217	0,38	0,34	0,23	0,21
56-273	—	0,31	0,19	0,20
56-274	—	0,45	0,24	0,28
petroleum coke	—	0,59	0,34	—

From Table VI, it is seen that there is a decrease in the specific surface areas of the cokes on heat treatment to 2 570 and 2 650 °C. At 2 650 °C, this decrease ranges from 50 % for sample 22 761 to 13 % for sample 22 763. The percentage decrease in surface area is seen to be roughly related to the surface area of the coke — the higher its area the greater the percentage decrease. This results in the surface areas of all graphitized carbons varying much less than the surface area of the cokes. This is analogous to the findings of WALKER and SEELY⁽¹⁵⁾, who found that the graphitization of graphite wear-dust, having areas ranging from 409 to 699 m²/g, reduced the areas to values ranging only from 82 to 91 m²/g.

Despite the over-all decrease in areas on graphitization, there is some indication that the specific surface area of the graphitized carbons increases slightly in going from 2 570 to 2 650 °C. Perhaps volatilization of some impurities in this temperature range produced slight porosity. It is noted that the surface area of the petroleum coke after graphitization at 2 570 °C is ca 25 % greater than the surface area of the graphitized pitch cokes.

E. Electrical Resistivities of Cokes and Graphitized Carbons.

Table VII presents electrical resistivity data on the cokes and graphitized carbons produced from both

the Group A and B coal tar pitches. The resistivities of the cokes are seen to be quite similar. Disregarding samples 22 761 and BD-PSU-5 (lignite pitch), the resistivities of the remaining pitch cokes vary by only ± 12 %. As expected because of a higher calcination temperature, the petroleum coke has a lower electrical resistivity than any of the pitch cokes.

TABLE VII

Electrical resistivities at 2 500 P.S.I. and 25 °C
For cokes and graphitized carbons.

Sample	Coke	Electrical Resistivity, ohm/cm	
		Graphitized Carbon	
		2 660 °C	2 680 °C
22 761	0,050	0,0081 ^(a)	—
22 763	0,038	0,0049 ^(a)	—
22 805	0,040	0,0042	0,0032
23 217	0,038	0,0029 ^(b)	—
56-273	0,038	0,0044 ^(a)	—
56-274	0,032	0,0029 ^(b)	—
BD-PSU-1	0,037	0,0032	0,0031
-2	0,035	0,0035	0,0034
-3	0,041	0,0046	0,0038
-4	0,038	0,0042	0,0032
-5	0,049	0,0050	0,0042
-6	0,036	0,0032	0,0030
-7	0,040	0,0030	0,0029
-8	0,038	0,0028	0,0025
-9	0,039	0,0037	0,0029
-10	0,037	0,0036	0,0027
-11	0,035	0,0031	0,0024
-12	0,037	0,0027	0,0026
-13	0,037	0,0034	0,0027
-14	0,040	0,0038	0,0031
-15	0,041	0,0039	0,0030
-16	0,034	0,0026	0,0023
-17	0,034	0,0020	0,0021
-18	0,032	0,0033	0,0023
-19	0,036	0,0035	0,0029
petroleum coke	0,024	0,0031	0,0025

^(a)Graphitized at 2 570 °C

^(b)Graphitized at 2 650 °C.

On graphitization, there is a marked decrease in the electrical resistivities of all samples. Further, as expected, the higher temperature graphitization run (*) produced, for each sample, the lower electrical resistivity. Or conversely, even though it is difficult to distinguish a 20 °C difference in temperature at a temperature level around 2 660 °C using an optical pyrometer, the resistivity data clearly confirm that the samples « heated to 2 680 °C » indeed did see a higher temperature than those « heated to 2 660 °C ». This is of importance when considering the reactivity results.

(*) It is noted that the majority of the Group A samples were graphitized at temperatures lower than those used for the Group B samples. Unfortunately, insufficient samples of the Group A cokes were available to make heat treatment runs at 2 660 and 2 680 °C.

F. Gas Reactivities of Cokes and Graphitized Carbons.

1. *Reactivities of cokes and graphitized carbons to CO₂ at 1 150 °C.* — Tables VIII and IX present data for the reactivity of cokes and graphitized carbons to CO₂ from the Group A and Group B pitches, respectively. Clearly, for the majority of the pitch samples, the reactivity of the carbons graphitized between 2 570 and 2 660 °C is greater than the reactivity of the cokes. Samples 56-274 (graphitized at 2 570 °C) and BD-PSU-2 are exceptions. For the Group A coal tar pitches, an increase in graphitization temperature from 2 570 to 2 650 °C results in a marked increase in reactivity of the carbons to CO₂. To the contrary, for the Group B coal tar pitches (and pitch 22 805 from Group A) an increase in graphitization temperature from 2 660 to 2 680 °C produces a decrease in reactivity, with two exceptions. These exceptions are samples BD-PSU-1 and -18.

TABLE VIII

Reactivities of cokes and graphitized carbons from group a pitches to carbon dioxide at 1 150 °C.

Sample	Weight Per Cent Burn-Off in Two Hour		
	Coke	Graphitized Carbon	
		2 570 °C	2 650 °C
—	—	—	—
22 761	8,7 ^(a)	16,2 ^(b)	29,3
22 763	9,8	12,4	24,4
22 805	8,8	15,0	26,2
23 217	7,4	17,6	24,3
56-273	7,6	12,4	31,1
56-274	22,0	15,9	27,0
petroleum coke	55,2	10,7	—

^(a) Reactivities on pitch cokes represent average of reactivities determined on individual samples from three different coking runs.

^(b) Reactivities on carbons at each graphitization temperature represent average of reactivities on two graphitized coke samples.

It is noted that the wide variation in reactivities of the pitch cokes to CO₂ is not carried over to the graphitized samples. For example, considering the Group B pitches, the cokes show a spread in reactivity from 3,5 to 30,8 % burn-off in two hours. On the other hand, exclusive of BD-PSU-5 (lignite pitch), the samples graphitized at 2 660 °C show a spread in reactivity from only 19,8 to 28,1 %.

An increase in reactivity of cokes from coal tar pitch and petroleum pitch to CO₂ upon graphitization has been reported previously by WALKER and NICHOLS ⁽⁵⁾. WALKER and RUSINKO ⁽¹⁰⁾ also reported that a graphitized carbon electrode had a higher gasification rate in CO₂ than four amorphous elec-

trodes. The present work not only agrees with the findings of the above authors but emphasizes the marked effect which relatively slight variations in graphitization temperature also can have on reactivities of carbons in CO₂.

TABLE IX

Reactivities of cokes and graphitized carbons from the group b pitches to carbon dioxide at 1 150 °C.

Sample	Coke	Weight Per Cent Burn-Off in Two Hours	
		Graphitized Carbon	
		2 660 °C	2 680 °C
—	—	—	—
BD-PSU-1	17,7 ^(a)	24,5 ^(b)	26,8
-2	30,8	21,1	20,5
-3	8,7	23,0	19,1
-4	5,0	22,9	12,3
-5	30,2	40,3	37,9
-6	16,8	20,1	14,4
-7	15,0	20,5	14,7
-8	11,3	24,3	16,8
-9	14,0	25,0	21,9
-10	8,1	19,8	14,2
-11	8,7	23,8	17,3
-12	6,6	23,6	15,1
-13	3,5	21,7	14,5
-14	16,7	28,1	17,2
-15	17,5	25,7	17,9
-16	14,4	25,1	15,2
-17	11,6	20,8	15,2
-18	12,4	20,0	25,5
-19	14,1	22,7	16,8
22 805	8,8	26,8	17,2
petroleum coke	55,2	22,5	15,2

^(a) Reactivities on pitch cokes represent average of reactivities determined on individual samples from two different coking runs.

^(b) Represents one reactivity run on one graphitized coke sample at each temperature in every case.

No correlation is found between the per cent ash in the coal tar pitches and the reactivity of the cokes produced therefrom. For samples containing essentially the same ash content, there is as much as a 250 % difference in reactivities.

For the Group A coal tar pitches, the reactivity data of the cokes (as a group) or graphitized carbons (as a group) in CO₂ cannot be explained on the basis of the surface area or crystallographic parameters of these materials.

In marked contrast to the increase in reactivity in CO₂ upon graphitization for the majority of the pitch samples, the petroleum coke is seen to undergo a major decrease in reactivity to CO₂ upon graphitization to 2 570 °C. However, the reactivity of the petroleum coke to CO₂ is seen to not fall continuously with increasing heat treatment temperature. The sample heat treated at ca 2 660 °C. has a markedly higher reactivity than does the sample heat treated to 2 570 °C.

2. *Reactivities of cokes and graphitized carbons from Group B pitches to air at 700 °C.* — Table X presents data for the reactivity of cokes and graphitized carbons from Group B pitches to air at 700 °C. In direct contrast to reactivity results in CO₂,

TABLE X
Reactivities of cokes and graphitized carbons from group b pitches to air at 700 °C.

Sample	Weight Per Cent Burn-Off in Two Hours	
	Coke	Graphitized Carbon, 2 660 °C
BD-PSU-1	27,8	12,8
-2	26,0	13,5
-3	26,5	9,8
-4	26,1	5,7
-5	24,5	19,8
-6	25,4	9,6
-7	24,2	9,5
-8	25,8	10,3
-9	25,6	9,3
-10	24,5	12,1
-11	25,9	10,0
-12	25,9	9,0
-13	27,2	13,8
-14	24,5	12,9
-15	24,3	15,3
-16	28,2	13,6
-17	27,8	13,8
-18	27,4	15,1
-19	25,4	11,9
petroleum coke	24,8	9,9

all of the graphitized carbons have markedly lower reactivities in air than do their coke counterparts. Also the reactivities of the cokes to air are strikingly similar; unlike the wide variation found for the reactivities of the cokes to CO₂. Reactivity results for the petroleum coke are of interest. As was the case for reactivity results in CO₂, graphitization decreases the reactivity of the petroleum coke. However, the reactivity of the petroleum coke to air closely agrees with the reactivities of the pitch cokes to air, whereas the reactivity of the petroleum coke to CO₂ is markedly higher than the reactivities of the pitch cokes to CO₂.

3. *Effect of heat treatment temperatures and atmosphere on the reactivities of a pitch coke and petroleum coke.* — Samples of pitch coke 56-273 and petroleum coke were heated at a series of temperatures in an induction furnace, as previously described. The atmosphere in the induction furnace consisted of either He or a 1 % Cl₂ — 99 % He mixture. Table XI summarizes the reactivity results. In agreement with previous findings where the resistance furnace was used to heat treat the samples, the reactivity of the pitch coke in CO₂ is seen to increase following heat treatment to higher temperatures. A maximum in reactivity is found following heat treatment to ca

2 000 °C. Another maximum (displaced to a higher temperature than found previously for sample 22 805) probably occurs at a temperature above 2 800 °C. Also as found before, the reactivity of petroleum coke to CO₂ shows a marked decrease upon heat treatment. The initial decrease is found to occur between the calcination temperature and a heat treatment temperature of 1 750 °C. A slight increase in reactivity is suggested with an increase in heat treatment temperature between 1 750 and 2 250 °C. This is followed by a second, sharp decrease in reactivity on heat treatment to 2 600 °C. No further maximum in reactivity is found for the petroleum coke following heat treatment at 2 825 °C, probably because the gap in heat treatment temperature is too large to uncover a maximum.

TABLE XI
Reactivities of carbons to carbon dioxide and air

Sample	Heat Treatment Temperature, °C	Weight Per Cent Burn-Off in Two Hours	
		Carbon Dioxide at Air at	
		1 150 °C	700 °C
Pitch 56-273	1 000	7,6	25,8
—	1 745	27,0	22,8
—	1 750 ^(a)	18,5	20,4
—	2 000	28,3	21,3
—	2 005 ^(a)	12,3	12,4
—	2 240	11,9	16,1
—	2 250 ^(a)	10,9	10,4
—	2 600	6,4	10,4
—	2 800	24,5	8,2
petroleum coke	1 250	55,2	24,8
—	1 750	34,4	22,5
—	2 020	34,9	20,6
—	2 005 ^(a)	34,6	6,0
—	2 250	37,0	16,2
—	2 265 ^(a)	34,6	6,4
—	2 600	10,6	—
—	2 825	11,0	14,4

^(a) Atmosphere in furnace 1 % Cl₂ — 99 % He.

The effect of heat treatment on the reactivity of pitch coke and petroleum coke to air is seen to be considerably different from the effect of heat treatment on their reactivities to CO₂. The reactivity of both these materials to air is seen to decrease progressively with increasing heat treatment temperature. Furthermore, the reactivities of the two materials to air for heat treatment temperatures up to 2 250 °C parallel each other closely.

Limited data in Table XI indicate that the success attained in decreasing carbon reactivity by heat treatment in a partial Cl₂ atmosphere (compared to a Cl₂-free atmosphere) depends upon the carbon, heat treatment temperature, and oxidizing gas.

used in the reactivity studies. For the CO_2 reaction use of a partial Cl_2 atmosphere during heat treatment of the pitch coke, off-sets, in part, the effect of heat treatment on increasing reactivity. For the air reaction, use of a partial Cl_2 atmosphere during heat treatment is found to augment the effect of increasing heat treatment temperatures in decreasing the reactivity of both the pitch coke and petroleum coke.

Discussion.

The marked difference in the effect of heat treatment temperature on subsequent reactivities to CO_2 of carbons derived from the coal tar pitches and petroleum coke is of importance. For the majority of the pitch cokes, an increase in reactivity upon graphitization occurs despite a decrease in surface area, a decrease in impurity content [because of the volatilization (¹⁷) of impurities], and an increase in crystallite size. It is a popular belief that such changes should decrease the reactivity of carbon. These results again confirm the fact that the total surface area is not the sole criterion determining gasification rates (^{5, 12, 13}). Long and SYKES (¹⁸) postulate that the top and bottom edge atoms of a carbon crystallite are the most reactive to gasification. From this, the conclusion is drawn that the smaller crystallites, with their higher concentration of edge atoms per unit weight, should be more reactive than the larger crystallites. However, this is not the case in the present work. Numerous workers have shown experimentally that the addition of impurities to carbon increases its reactivity. Despite a much greater concentration of impurities in the pitch cokes than in the graphitized carbons, the reactivity of the majority of the pitch cokes to CO_2 is lower.

In agreement with conventional theories, the reactivity of the petroleum coke to CO_2 markedly decreases on heat treatment to 2 570 °C. However, again the situation is seen to be complex; for an increase in reactivity is noted upon increasing the heat treatment temperature from 2 570 to 2 660 °C.

It is suggested that reactivity to CO_2 is determined primarily by the nature of the metallic impurities in the carbon and their degree of association with the carbon matrix. A metallic impurity in close association with the carbon matrix can effect the distribution of electrons in the matrix by accepting an electron (transition metal) or by forming a covalent bond (alkali metal). [LONG and SYKES (¹⁹) have discussed at some length a model in which electronic interaction between carbon and a catalyst facilitates the individual stages of carbon gasification.] A low temperature carbon may have

a substantial impurity content; but if the impurities are not in the right location or chemical combination to effect electron transfer within the carbon, they will serve as ineffective catalysts. However, when the carbons are heat-treated to higher temperatures, solid-state diffusion of the impurities along the boundaries of carbon crystallites and reaction of the impurities with the carbon matrix is made possible. Thus, an ineffective catalyst may be converted into an effective one. Furthermore, the carbon crystallites grow with increasing heat treatment temperature, which means that a given impurity atom can be effective at catalyzing more carbon atoms because of the good electron-transfer properties across the basal planes of carbon crystallites. As the temperature is increased, some of the impurities are volatilized away so that at each temperature the effect of the impurities on catalyzing the reaction depends upon three parameters — the amount of the impurities, their location with relation to the carbon matrix, and the carbon crystallite diameter. Finally, at sufficiently high temperature the impurity content is depleted to such an extent that the reactivity of the carbon would be expected to reach a maximum and then decrease. Obviously, individual impurities with their different rates of solid state diffusion through the carbon matrix, different vapor pressures, and different rates of interaction with the carbon, would be expected to be affected differently by temperature. Therefore, a series of reactivity maxima over the range of heat treatment temperature, associated with different impurities, is conceivable.

For the majority of the coal tar pitch samples, the reactivity data in CO_2 are explained as follows: Cokes produced from the pitches consist of two phases — a major, high-purity phase from the organic fraction of the coal and a minor, low-purity phase originating from entrained solids from the coke oven. The reactivity of the high-purity phase to CO_2 is low and the reactivity of the low-purity phase is high. The over-all reactivity of the coke is relatively low because of the small amount of low-impurity material present. Upon heat treatment, temperatures are reached where solid-state diffusion of the impurities from the low-purity carbon into the high-purity carbon becomes appreciable (doping occurs). A more uniform sample of intermediate purity is produced, which has a higher over-all reactivity to CO_2 , because all (or the majority) of the carbon has an appreciable reactivity. At higher heat treatment temperatures, the impurity content of the carbon (because of continued volatilization) is depleted to such an extent that loss of impurities becomes dominant over distribution of impurities and the reactivity begins to decrease.

For pitch 22 805, the larger increase in reactivity

after heat treatment in the temperature range 2 570 to 2 660 °C than in the range 1 150 to 2 570 °C indicates that increase in crystallite size is not the dominant factor affecting reactivity in CO₂, since an appreciably greater increase in crystallite size occurs in the latter temperature range. Apparently, the rate of solid state diffusion of some catalytic impurities (impurity) becomes significant in the higher temperature range.

The CO₂ reactivity data for the heat treated petroleum coke are explained as follows: Petroleum coke produced from the delayed coking process is essentially a one-phase system. As a consequence, the extent to which the sample is additionally doped by heating to higher temperatures is overshadowed by the decrease in concentration of low-boiling-point impurities, which apparently contribute to catalyzing the reactivity of the the coke. Some subsequent increase in reactivity upon heat treatment at higher temperatures apparently is related to more intimate contact and compound formation of higher-boiling-point impurities with the carbon matrix.

It is thought significant that WALKER and NICHOLS⁽⁵⁾ found the reactivities of both coal tar pitch coke and petroleum pitch coke in CO₂ to increase upon graphitization. It is suggested that the majority of impurities present in a coke produced from a material which has been volatilized from the source material (whether coal or petroleum) is not in as intimate contact with the carbon matrix as impurities which remain behind with the residue (as with delayed petroleum coke, for example). In the former case, the majority of the impurities are present because of entrainment of some relatively impure material. Hence, the effect of heat treatment of the coke at higher temperatures on subsequent reactivity to CO₂ will be markedly different, depending upon how the coke was produced.

Results for the reactivity of pitch cokes in air indicate that the explanation for the reactivity results of the pitch cokes in carbon dioxide is not complete. That is, the reactivity of the pitch cokes to air continuously decreases with increasing heat treatment temperature. It is suggested that at least two additional factors need be considered to explain qualitatively the reactivity results: (1) whether the reaction is exothermic or endothermic and (2) what happens to the thermal conductivity of carbon crystallites as they increase in size, perfection, and purity. For an endothermic reaction, a new reaction center, produced by the removal of a carbon-oxygen complex from the surface should initially be cooler than the majority of the carbon atoms in the crystallite. On the other hand, for an exothermic reaction, a new reaction center should initially be hotter than the majority of the carbon atoms in the crystallite. At reaction temperatures used in this work, the rate of

return of the new reaction centers to the steady-state temperature will be primarily dependent upon the thermal conductivity of the carbon (*). If the new reaction center returns to the steady-state temperature before a reacting gas molecule collides with it, the resulting reaction rate will be that corresponding to the steady-state temperature. Otherwise, the reaction rate will be lower or higher than that corresponding to the steady-state temperature depending upon whether the new reaction center has been heated or cooled.

It is suggested that for graphite, which has a relatively high thermal conductivity, the majority of new reaction centers return approximately to the steady-state temperature before collision of a reacting gas molecule occurs. On the other hand, for coke, which has a much lower thermal conductivity than graphite, it is suggested that the majority of new reaction centers do not return to their steady-state temperature before collision of a reacting gas molecule occurs. As a result, for the coke — CO₂ reaction, the majority of the new reaction centers are at a lower temperature than is the case for the graphitized coke — CO₂ reaction. This fact would make the « apparent » reactivity of the coke less than that of the graphite. On the other hand, for the carbon-air reaction, the majority of the new reaction centers of the coke would be at a higher temperature than those of the graphitized coke. In this case, the « apparent » reactivity of the coke would be greater than that of the graphite.

In conclusion, it is suggested that for carbons which do not change appreciably in surface area upon heat treatment (as in the present case) the following factors can be of importance in determining changes in reactivity of the carbon to oxidizing gases with heat treatment:

1. Total impurity content.
2. Uniformity of impurity distribution in the carbon matrix.
3. Nature of impurities and their chemical form in the carbon (that is, oxides, carbides, etc.).
4. Ratio of basal plane to edge surface area.
5. Carbon crystallite size.
6. Thermal conductivity of the carbon, and
7. Whether reaction is endothermic or exothermic.

Unfortunately, in most carbons factors 1 to 6 are known with varying degrees of uncertainty, and predictions of relative reaction rates of different carbons to oxidizing gases is not possible.

(*) This problem is analogous to the consideration of « thermal spikes » in nuclear reactors, where the solid is bombarded with fast neutrons. Atoms in the vicinity of the thermal spike are heated to temperatures considerably above the steady-state temperature for short periods of time.

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DISCUSSION

Bond. — It appears from C. R. KINNEY's paper that much of the reactivity of carbons produced from coal tar pitches results from the mineral impurities in them. Can C. R. KINNEY comment upon the possibility of using coal extracts, which are substantially mineral free, as the starting material for carbon production and does he think the graphitised product would be of low reactivity?

C. E. Kinney. — We have done nothing on pitch extracts. This would be interesting because it would eliminate a large part of the mineral matter before charring and coking the material.

J. Parisot. — A propos des taux de bore page 88, tableau II. Certains sont très faibles.

1° Les brais ont-ils été traités spécialement?

2° Quelle est la méthode d'analyse utilisée?

C. R. Kinney. — The trace elements were determined spectrographically on the ashes obtained from the pitches.

I can't say why the boron content of most of the pitches is low. The pitches were not treated to lower the boron content.

Berenbaum. — The suggestion is made in this paper that the differences observed in reactivity between cokes and graphitised carbon may be partly due to their different thermal conductivities. We know that under nuclear irradiation there are very large changes in thermal conductivity. As far as a reaction with oxygen is concerned, by the arguments put forward in the paper, a lower conductivity would rise the reactivity as observed (although, of course, there are many other factors which have the same effect — introduction of imperfections, etc...). For the CO₂ reaction lower conductivity would mean lower reactivity and this might be distinguished, although in competition with the other effects referred to.

C. R. Kinney. — Personally I don't think we know enough about the mechanism of oxidation by either carbon dioxide or oxygen to say whether thermal conductivity through the carbon structure is a controlling factor or not. No doubt once an oxidative reaction starts it continues more easily at that point than in the unattacked layers.

G. R. Hennig. — The change in thermal conductivity of graphite which is caused by neutron bombardment is very large at room temperature. However, if the samples are heated to the temperature at which the reaction with CO₂ is carried out, most of this damage anneals out. It therefore seems unlikely that appreciable temperature gradients would be set up within the irradiated graphite during reaction with CO₂. We have carried out preliminary experiments on the inter-action of CO₂ with irradiated single crystals which suggest that the kinetics of the reaction are very appreciably altered by irradiation.