

CARBONS PRODUCED FROM KNOWN ORGANIC COMPOUNDS

II.*—Anthracene–biphenyl and phenanthrene–biphenyl systems

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Binary mixtures (systems) of typical graphitisable and non-graphitisable hydrocarbons were carbonised and heat treated to study the graphitisability of the resulting carbons. The hydrocarbons selected were anthracene, phenanthrene and biphenyl. The first two are isomers and are highly graphitisable; biphenyl is non-graphitisable. Carbonisations were carried out in a pressure vessel containing either anthracene–biphenyl or phenanthrene–biphenyl mixtures at 73–98 atm and 550°. The resulting chars were dried, ground, calcined at 950° to form a coke, then heat treated at 2800°. These carbons were studied by optical microscopy, X-ray diffraction, helium density, and electrical resistivity measurements. For the anthracene–biphenyl system, carbons of homogeneous texture were not produced; rather fractions of highly graphitic and poorly graphitic carbons were obtained. For the phenanthrene–biphenyl system, carbons which are more homogeneous on a macro-scale were produced, their graphitic character decreasing sharply as the amount of biphenyl in the original mix was increased.

Introduction

Part I of this series¹ reported that cokes derived from the carbonisation of anthracene, phenanthrene and their mixtures were all highly graphitisable. This paper describes results obtained when these materials are carbonised together with the non-graphitisable compound biphenyl. Biphenyl was reported as a compound having poor graphitisability by Milliken² and Kinney.^{3–5}

Many aromatic compounds were studied individually in the condensed phase by Union Carbide's Carbon Products Division.⁶ These studies showed that if the molecular structure is planar (fused rings), the compound will probably graphitise; but if the original molecule is non-planar or if non-planar intermediates are formed, the material may be non-graphitisable. This explanation adequately describes the behaviour of the three compounds used as starting materials in this study.

For convenience, Table I lists the significant properties of these starting materials. It should be noted that the structural isomers anthracene and phenanthrene have fused rings and planar geometry; these are graphitisable. Biphenyl is an aromatic hydrocarbon able to undergo rotation about the inter-ring bond, making it non-planar and non-graphitisable.

Experimental

Preparation of the 950° cokes and 2800° carbons

Starting materials

All of the starting materials were obtained from Rütgers-werke and Teerverwertung A.-G., Duisburg-Meiderich, Germany. The anthracene was of specified

99% purity and had an observed sealed capillary tube melting point of 216–217°. The phenanthrene was specified to be sulphur-free and of 98% purity. The observed capillary tube melting point was 98–100°. The biphenyl was of specified 98% purity and had an observed capillary tube melting point of 68·5–70·5°. No attempt was made to further purify these materials.

Pressure vessel

The pressure vessel (American Instrument Company, Silver Spring, Maryland) was constructed of chrome–vanadium steel and measured 4 3/8 in o.d. × 2 9/16 in i.d. × 21 in inside depth, with a capacity of 1780 ml. It was bolted into an electrical heating jacket mounted on a mechanical shaking mechanism (American Instrument Company). Nitrogen was introduced into the vessel to displace air.⁷

Temperature control in the pressure vessel

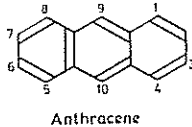
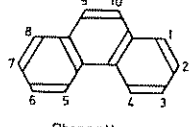
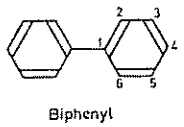
A thermocouple was inserted in the heating jacket. This was connected to a Leeds & Northrup Speedomax G recorder, equipped with a controller. The bulk temperature was monitored with a second thermocouple inserted in the vessel thermowell.

The bulk heating rate was set to increase linearly at 1 deg./min from 60° to 550°, at which point the soak period automatically started. The soak period was varied for the different samples from 7 to as long as 18 h depending on the rate of reaction. After the reaction was largely complete (as shown by a near zero slope in the pressure–time curve), power was shut off. Biphenyl, however, never reached constant pressure, so the soak period was an arbitrary 16·3 h in run 2. The assembly was then allowed to cool to about 30° with the aid of a small fan; this cooling generally required 12 h. The contents of the pressure vessel could then be easily removed.

* Part I: *Carbon*, 1967, 5, 13

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TABLE I
Properties of starting materials

Structural formula and numbering scheme	 Anthracene	 Phenanthrene	 Biphenyl
Empirical formula	C ₁₄ H ₁₀	C ₁₄ H ₁₀	C ₁₂ H ₁₀
Molecular wt, g/mol	178.2	178.2	154.2
Melting point, °C	218	100	70
Normal boiling point, °C	342	340	255
Origin	Coal tar contains 1.1%	Coal tar contains 4.0%	Produced from benzene at 750°C
Family	Polynuclear aromatic fused-ring hydrocarbon	Structural isomer of anthracene	Polynuclear aromatic hydrocarbon
Geometry	Flat	Flat	Possible rotation about the inter-ring bond

Method used to calculate gas generation in the pressure vessel

An indication of the amount of gas evolved during pyrolysis in the pressure vessel was obtained by calculating the ratio of moles of gas evolved to moles of reactant charged, n_g/n_c . The moles of gas evolved were calculated from the ideal gas law using the pressure and temperature at the end of the cooling period.

Drying and calcining

The furnace used for drying and calcining the samples was a Hoskins 1870W tube furnace with a 2 in o.d. \times 3 ft length of quartz tube. Pre-purified grade N₂ was passed at > 2 l/min through a drying train and a de-oxidising furnace before passing into the quartz tube. Temperature measurement and control were effected with a single Inconel-sheathed thermocouple positioned in the sample zone and connected to a recorder-controller. In all cases, the heating rate was 5°/min, and the soak time was 2 h. The soak temperature was 300° for drying and 950° for calcining. Cooling required about 12 h.

Drying of samples was accomplished by pulverising the material and loading about 140 g directly into the quartz tube, tamping it entirely within the heated section. Calcining of 24 g samples was performed in a small Vycor boat placed inside the quartz tube.

Graphitising

The furnace used for graphitising was a graphite-resistance type furnace manufactured by Richard D. Brew & Co., Inc., Concord, New Hampshire. It had a cylindrical sample holder 3 in dia. \times 6 in high, machined from graphite. About 8 g of the powdered samples could be introduced into each of six holes in the sample holder. An optical pyrometer was sighted through a

prism and a quartz window into a central hole in the sample holder. It was necessary to clean carbon deposits from the quartz window before each reading. A Leeds & Northrup optical pyrometer was used having three ranges above 760°. Corrections were applied to the readings to convert brightness temperature to true temperature. Argon was circulated through the furnace at 8 ft³/h and at 1 atm pressure. The furnace was controlled manually. The heating and cooling rates were linear at 15.5°/min from 800–2800°. The soak period and soak temperature were 0.5 h at 2800° in all cases.

Characterisation of the 950° cokes and 2800° carbons

X-ray diffraction measurements

X-ray diffraction measurements were made on the 2800° carbons in the laboratories of Airco Speer using a General Electric XRD-5 unit emitting Cu α radiation through a 0.7 mil Ni filter with the tube operating at 16 mA and 50 kV. 20–65% KCl was used as an internal standard. Some samples required addition of collodion–amyl acetate to keep them suspended in the open frame holder. Materials that were graphitic were measured using the (004) diffraction peak. Materials that were still ‘hard carbons’ were measured from the (002) peak. Measurements were made of the interlayer spacing, the crystallite height or L_c , and the relative intensity of the (002) peak.

Optical microscopic examination

Optical microscopic photographs were made at Airco Speer by introducing a few mg of the 200 \times 325 mesh cokes in an amber-coloured epoxy resin (HYSOL RB-2038, Hysol Corp., Olean, New York) with the necessary curing agent in a cylindrical mold and removing air bubbles under vacuum. When cured, a solid matrix was formed, one surface of which was ground

optically flat. This surface was photographed through a Leitz Panphot Metallograph using 500 \times magnification and reflected polarised light.

Helium density measurements

Helium densities of the 42 \times 65 mesh cokes and 2800 $^{\circ}$ carbons were measured using the constant pressure helium densitometer constructed by W. Stacy and described in detail by Bessant.⁸

Resistivity measurements

Electrical resistivities of the cokes and graphites were measured on 2 g samples of 42 \times 65 mesh material. 7000 lb/in² was hydraulically applied to the sample during measurement. The apparatus was described by Baumbach.¹⁰

Results

Preparation of the cokes

Table II shows experiment identification numbers, the charge introduced into the pressure vessel, the amount of recovered char and tar, soak time, maximum pressure, residual pressure, and temperature after cooling. The char (solid residue removed from the pressure vessel) recovery reflects some tar content and handling loss, as well as the extent of conversion to solid carbon. Tars are viscous dark liquids, most of which are produced by biphenyl, as shown in run 2. The overall coke yield was

calculated from the weight of solid residue remaining after the char was dried at 300 $^{\circ}$ and calcined at 950 $^{\circ}$.

Characterisation of the 950 $^{\circ}$ cokes and 2800 $^{\circ}$ carbons

Optical microscopic examination

Photomicrographs of the calcined cokes are shown in Figs 1 and 2. The particle size of the coke is 200 \times 325 mesh (44–74 μ m) and the original photographs were taken using 500 \times magnification. The dark areas in these photographs are the epoxy resin.

The anthracene–biphenyl system is shown in Figs 1(a)–1(d) in order of increasing initial biphenyl concentration in the pressure vessel. Fig. 1(a) shows the coke resulting from pure anthracene, which has smooth curved surfaces, many flow lines resulting from shear forces acting on a viscous mass, and the fissures resulting from gas evolution. At the opposite extreme, Fig. 1(d) shows the coke produced from pure biphenyl. It appears to have a smooth and flat 'glassy' surface free from flow lines and fissures with a few pinholes. Fig. 1(b) shows the coke produced from a 25% biphenyl–75% anthracene mixture. Three distinct types of particles are visible. The particle labelled 1 resembles the anthracene coke. Particles 2 and 3 have rough surfaces. Fig. 1(c) depicts the coke which results from a 50% mixture. Three recognisable kinds of particles are present; the pure anthracene particle 1, the pure biphenyl particle 2, and an intermediate particle 3 resembling 2 in Fig. 1(b).

TABLE II
Charges, yields, and process conditions

Run No.	Charge, g		Recovery			Soak time at 550 $^{\circ}$ C, h	Max. pressure at 550 $^{\circ}$ C, lb/in ² (gauge)	Residual pressure and temperature	
			Char, g	Tars, g	Overall coke yield, %			lb/in ² (gauge)	$^{\circ}$ C
1	200	Anthracene	166.4	0	80	7	1420	560	90
2	250	Biphenyl	133.4	63.6	41	16.3	1060	55	200
3	250	Phenanthrene	217.6	0	84	17.2	1110	52	410
4	100 100	Phenanthrene Biphenyl	161.7	—	68	18	840	245	55
5	125 125	Phenanthrene Biphenyl	184.2	20.5	61	18†	950	240	30
6	125 125	Anthracene Biphenyl	144.0	30.9	52	18	1100	*	*
7	187.5 62.5	Anthracene Biphenyl	160.1	14.1	58	18	*	*	*
8	187.5 62.5	Phenanthrene Biphenyl	173.3	4.2	57	18	950	290	25
9	225 25	Phenanthrene Biphenyl	204.6	0	68	18	975	325	41
10	237.5 12.5	Phenanthrene Biphenyl	201.7	0	69	18	940	310	35

* Clogged line to pressure gauge

† Mixed for 24 h at 300 $^{\circ}$ C before charring

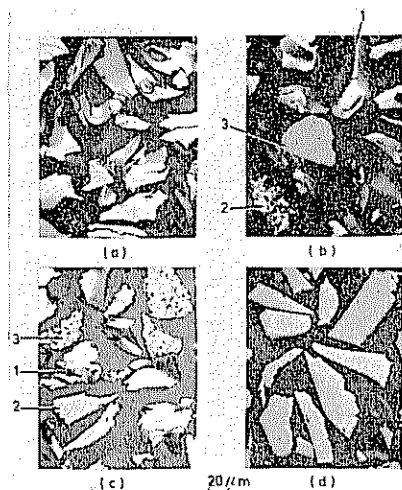


Fig. 1. Photomicrographs of cokes from the anthracene-biphenyl system

(a) Pure anthracene; (b) 75% anthracene-25% biphenyl; (c) 50% anthracene-50% biphenyl; (d) pure biphenyl

The second system examined was the phenanthrene-biphenyl system. Fig. 2(a) shows the coke obtained from pure phenanthrene. It is also characterised by curved surfaces, flow lines, and fissures. Fig. 2(b) shows the effect of adding 5% biphenyl to the phenanthrene. The particles labelled 1 resemble those of Fig. 2(a) while particle 2 resembles those of Fig. 2(c). Particle 3 may be a biphenyl particle. Its presence is anomalous. Figs 2(c) and 1(d) show the effect of addition of 10% and 25% biphenyl respectively. The higher concentration produces a graduation in particle appearance. The resemblance between particle 1 in Fig. 2(d) with the particles in Fig. 2(c), and particle 2 of Fig. 2(d) with particle 3 of Fig. 1(b) should be noted. At 50% biphenyl (Fig. 2(e)) a marked transformation to 'glassy' particles results.

Both anthracene coke and phenanthrene coke have the appearance of 'delayed coke'. Delayed coke is petroleum coke made by the delayed coking process, and it is known to produce excellent, anisotropic graphite. The 90% phenanthrene-10% biphenyl coke (Fig. 2(c)) has more the appearance of 'pitch coke' because it resembles the coke generally resulting from the coal tar pitch - a less ordered, more isotropic variety of carbon. Biphenyl coke is termed 'glassy' meaning a poorly ordered, completely isotropic, hard carbon, normally incapable of producing graphite. Making use of this terminology, the microscopic results are summarised in Table III.

X-ray diffraction studies

The interlayer spacing is plotted *versus* starting composition in Fig. 3. The broken lines indicate uncertainty. It may be seen that at least 25% by weight biphenyl may be tolerated in the anthracene without affecting the interlayer spacing of the highly graphitised component. However, in the phenanthrene-biphenyl

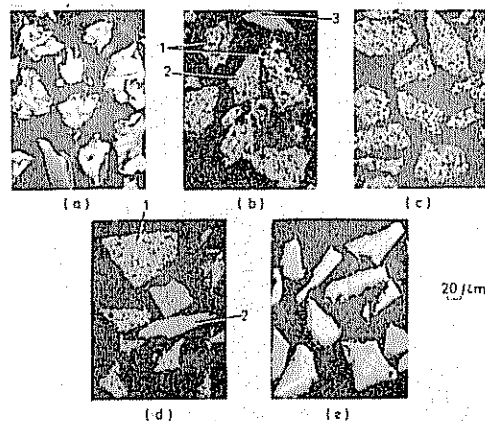


Fig. 2. Photomicrographs of cokes from the phenanthrene-biphenyl system

(a) Pure phenanthrene; (b) 95% phenanthrene-5% biphenyl; (c) 90% phenanthrene-10% biphenyl; (d) 75% phenanthrene-25% biphenyl; (e) 50% phenanthrene-50% biphenyl

system, an entirely different effect is observed. As little as 5% biphenyl produces a marked increase in interlayer spacing.

Table IV presents values tabulated as a function of starting composition for both systems. There is clearly a sharp drop in L_c with the addition of as little as 5% biphenyl to phenanthrene. This does not occur in the anthracene-biphenyl system. It should be emphasised, however, that whereas the diffraction arises from essentially the entire one phase system for the phenanthrene-biphenyl carbons, the diffraction is expected to arise primarily from the more graphitic phase for the heterogeneous anthracene-biphenyl carbons. Certainly diffraction from the glassy phase would hardly be in evidence for samples containing a significant graphitic phase.

If a powdered sample is placed on an X-ray slide, the intensity of the (002) peak is a function of the number of graphitic layer planes oriented parallel to the slide. The greater the intensity of the (002) peak, the greater the extent of crystallite alignment.¹¹ Fig. 4 depicts the relative intensity of the (002) peak as a function of initial biphenyl content for both systems. The presence of KCl no doubt affects the shape of the curves, but certain observations can be made. The relative crystallite orientation of the anthracene-biphenyl system is unaffected with increasing biphenyl concentration in the range studied (i.e., up to 50%). The portion of the curve above 50% is broken because of insufficient data. The phenanthrene-biphenyl system shows a sharply decreasing alignment of the crystallites, as the biphenyl concentration is increased.

Relationship of gas generation to interlayer spacing

Fig. 5 shows a plot of interlayer spacing of the 2800° carbons *versus* the ratio n_g/n_c (residual moles of gas/mole

TABLE III
Phase transformations in cokes

Fig.	Starting composition	No. of phases observed	Description of phases
I(a)	Anthracene	1	Delayed
I(b)	25% Biphenyl-75% anthracene	2	Delayed, Pitch
I(c)	50% Biphenyl-50% anthracene	3	Delayed, Pitch, Glassy
I(d)	Biphenyl	1	Glassy
2(a)	Phenanthrene	1	Delayed
2(b)	5% Biphenyl-95% phenanthrene	1	Pitch*
2(c)	10% Biphenyl-90% phenanthrene	1	Pitch
2(d)	25% Biphenyl-75% phenanthrene	1	Pitch
2(e)	50% Biphenyl-50% phenanthrene	1	Glassy
1(d)	Biphenyl	1	Glassy

* One glassy particle was also observed

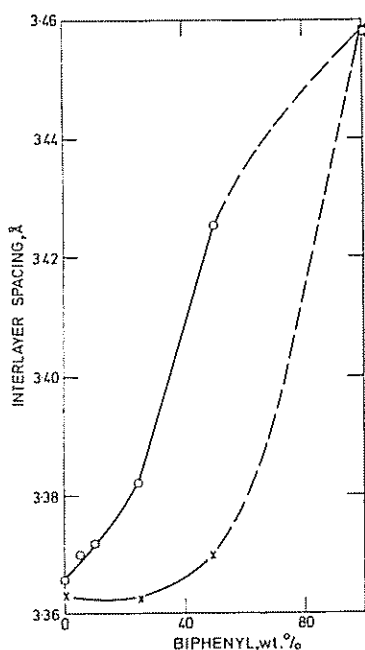


Fig. 3. Variation of interlayer spacing of 2800°C carbons with starting composition of anthracene-biphenyl and phenanthrene-biphenyl systems

○ Phenanthrene; × anthracene

charged) for both systems. Owing to clogged lines, the datum point for 25% biphenyl-75% anthracene is not shown and that for 50% biphenyl-50% anthracene was estimated from pressure readings at 550° which were extrapolated to 30°. The two points at 3.366 and 3.363 Å are for the pure phenanthrene and pure anthracene, respectively. The scattered point is from run 4.

Helium densities

Fig. 6 shows helium densities as a function of biphenyl content for both cokes and 2800° carbons in the anthra-

TABLE IV
Crystallite heights of 2800°C carbons

Starting composition	Run No.	L_c , Å	
		(002)	(004)
Anthracene	1	> 1000	946
25% Biphenyl-75% anthracene	7	> 1000	841
50% Biphenyl-50% anthracene	6	> 1000	540
Phenanthrene	3	988	420
5% Biphenyl-95% phenanthrene	10	494	252
10% Biphenyl-90% phenanthrene	9	432	199
25% Biphenyl-75% phenanthrene	8	216	130
50% Biphenyl-50% phenanthrene	4	71	—
50% Biphenyl-50% phenanthrene	5	72	—
Biphenyl	2	35	—

cene-biphenyl system. Fig. 7 shows the same information for the phenanthrene-biphenyl system. The cokes increase in density and the 2800° carbons decrease in density as the starting concentration of biphenyl is increased for both systems.

Electrical resistivity

The electrical resistivity of the 950° cokes and 2800° carbons from both systems are presented in Fig. 8. An arbitrary pressure of 7000 lb/in² was applied to the samples. The large decrease in resistivity when the cokes were subjected to the 2800° graphitisation temperatures can be seen.

Discussion

Formation of coke phases

The coke phases have been described as delayed, pitch, or glassy depending on whether they produce highly anisotropic, slightly anisotropic, or isotropic graphite. These phases may be produced by a combination of different reaction rates, solubility effects and free radical interactions during the carbonisation step.

Tilicheev, using an iron pressure vessel at 450°, reported

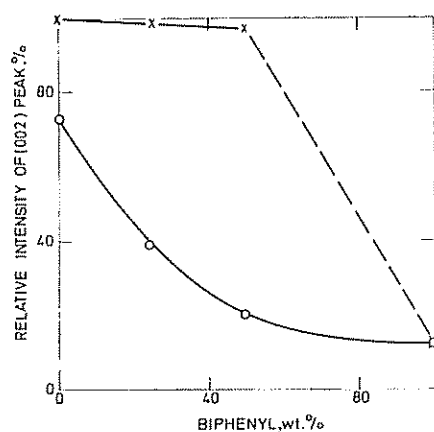


Fig. 4. Change in relative crystallite orientation of 2800°C carbons with the starting composition of the anthracene-biphenyl and phenanthrene-biphenyl systems
○ Phenanthrene; × anthracene

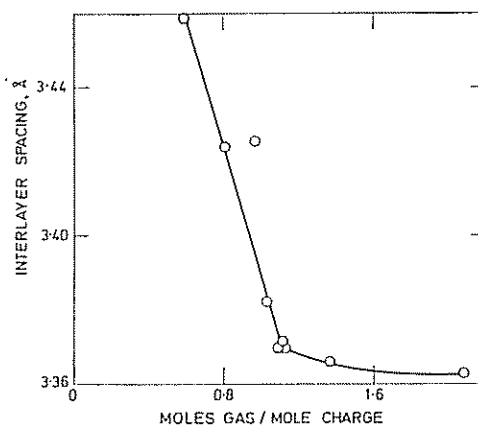


Fig. 5. Dependence of interlayer spacing of 2800°C carbons on gas generation during charring in anthracene-biphenyl and phenanthrene-biphenyl systems

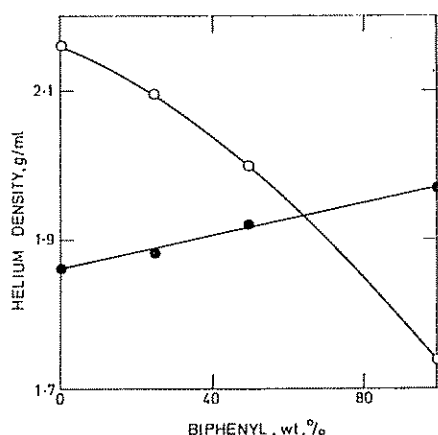


Fig. 6. Change in helium density of 950°C (●) coke and 2800°C (○) carbon with the starting composition of the anthracene-biphenyl system

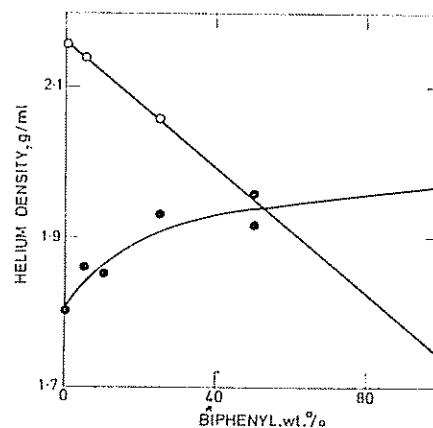


Fig. 7. Change in helium density of 950°C (●) coke and 2800°C (○) carbon with the starting composition of the phenanthrene-biphenyl system

first-order rate constants for the cracking of hydrocarbons (Table V).¹² Also shown in this Table are the ratios of the rate constants with respect to biphenyl, and the half lives calculated by $t_{1/2} = \ln 2/k_1$. From Table V it can be surmised that, in a 50% phenanthrene-biphenyl solution, both components will carbonise at about the same rate. However, in a 50% anthracene-biphenyl solution, the anthracene, being 1200 times greater in reactivity, carbonises and precipitates out of the biphenyl. Eventually, the biphenyl also chars.

The photomicrographs of the phenanthrene-biphenyl cokes (Fig. 2) are single phase, consistent with the above reading. The photomicrographs of the anthracene-biphenyl cokes (Fig. 1) clearly show anthracene coke particles separated from biphenyl coke particles, also in accord with the above reasoning.

Biphenyl is entirely gaseous at 550° since its critical temperature is 528°.¹³ This was confirmed by observing a sealed glass tube containing biphenyl at 550°*. Ob-

* Thus, the char produced from biphenyl is a kind of low temperature, high pressure pyrolytic carbon

servations in similar tubes, using an initial concentration at 600 g/l, clearly show that 50% anthracene-50% biphenyl and 50% phenanthrene-50% biphenyl mixtures are initially liquids, completely miscible and of low viscosity. Apparently, a gas-in-liquid solution exists at this concentration.

It is reported that phenanthrene is more soluble in common organic solvents than is its isomer, anthracene.¹⁴ Therefore, phenanthrene above its melting point may also be a better solvent than anthracene. In accordance, phenanthrene is reported to dissolve bituminous coal at 350° while anthracene apparently does not.¹⁵ This behaviour of phenanthrene suggests that it may be a greatly superior solvent for biphenyl as well as other species produced during carbonisation, compared to anthracene.

For a system of equal parts anthracene and biphenyl being heated up from about 300° at 1°/min with agitation, both are liquids completely soluble in each other. Free radicals form in both materials^{6, 16-19} but much faster in anthracene. At 450° the reaction is 1200 times faster than in biphenyl. Some of the anthracene free radicals

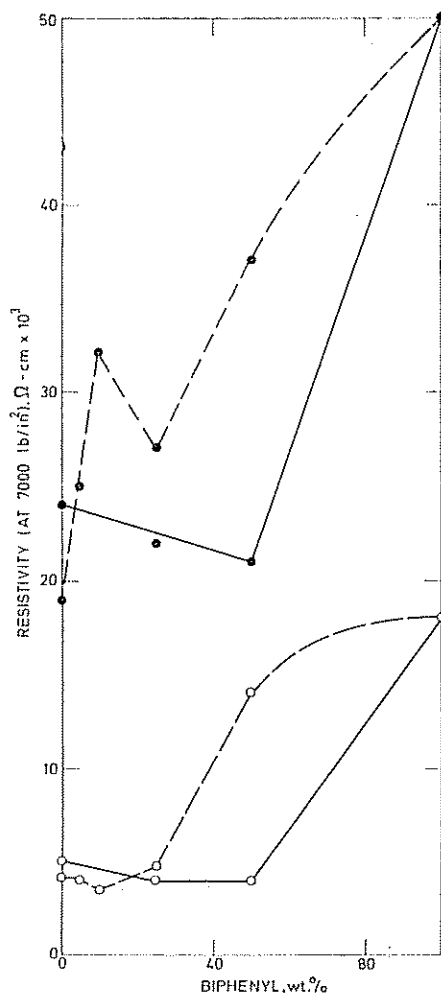


Fig. 8. Change in electrical resistivity of 950°C (●) cokes and 2800°C (○) carbons with the starting composition of the anthracene-biphenyl and phenanthrene-biphenyl systems

— Anthracene; - - - phenanthrene

may react with the biphenyl producing an adduct such as 4-(9-anthryl)-1-phenylbenzene, which may then polymerise with other free radicals. Other anthracene radicals condense with anthracene molecules to produce a char phase which precipitates out of solution. At 550° almost all of the anthracene has either reacted with biphenyl or condensed with itself. The biphenyl adduct will char to form a second copolymer-type phase. Finally free radicals form in the remaining biphenyl and a third phase ensues from the thermal polymerisation of biphenyl.

Graphitizability in anthracene-biphenyl system

It is clearly shown by X-ray diffraction and relative intensity data (Figs 3 and 4), by the crystallite heights (Table IV), helium densities (Figs 6 and 7), and electrical resistivities (Fig. 8) that in every case the carbons produced from the anthracene-biphenyl system are more

TABLE V

Tilicheev's first-order kinetic rate constants for cracking of hydrocarbons at 450°C.¹²

Compound	k_1, sec^{-1}	Ratio	$t_{1/2}$
Anthracene	3.2×10^{-4}	1200	36 min
Phenanthrene	8.7×10^{-7}	3.2	9 days
Biphenyl	2.7×10^{-7}	1	1 month

graphitizable than those produced from the phenanthrene/biphenyl system, for a given biphenyl concentration. This can be explained as follows. If the biphenyl concentration is initially low, the coke consists of pure anthracene coke and probably a small amount of anthracene-biphenyl copolymer. If biphenyl concentration is initially high, anthracene coke, anthracene-biphenyl coke, and biphenyl coke are formed (Fig. 1(c)). Anthracene coke is highly graphitizable, biphenyl coke is definitely not graphitizable, and the anthracene-biphenyl coke is somewhat intermediate, depending on the relative portion of its two components. Cornuault and co-workers have shown that when a graphitizable carbon is bound to a non-graphitizable one, an interaction can occur that enhances the graphitization of the latter.²⁰ Thus a non-linear variation in graphitizability with changing biphenyl content is observed in this system (Fig. 3).

In the phenanthrene-biphenyl system, since both molecules can form free radicals at roughly the same rate, they interact with each other. Possibly, the greater solubility of biphenyl gas in phenanthrene may be an important factor. The homogeneous copolymer that ensues is the single pitch coke phase of Figs 2(b)-(e). Since there is a single phase, the graphitizability is more nearly linear with changing biphenyl content (Fig. 3). This copolymer has non-planar structures built in and will always be less graphitizable for a given biphenyl concentration than will the multiple-phase cokes from the anthracene-biphenyl system.

The formation of several coke phases seems to cast off non-planar structures from the graphitizable phase and improve the graphitizability of the anthracene-biphenyl system, as opposed to the phenanthrene-biphenyl system.

Relationship of gas generation to interlayer spacing

In the polymeric char formed at 550°, supposedly there may exist benzene rings as found in biphenyl, fused rings as found in anthracene, and crosslinking. Disordered structures are produced when biphenyl-like linkages are able to rotate and bend about the C-C inter-ring bond. Fused rings would be less likely to rotate or bend, clearly producing more coplanar structures.

For a collection of small molecules undergoing thermal condensation to produce the graphite lattice, each molecule that reacts can form n bonds and release $n/2$ moles of hydrogen where $n = 1, 2, 3, \dots$. If $n = 2$, polymerisation continues but rotation of the molecules is possible. If $n = 3$, rotation stops and a coplanar macromolecule is more probable. If cracking occurs, parts of the molecule are destroyed; but these are probably strained rings, side chains, and bridgeheads which could not contribute to a graphitic structure. Cracking does, however, release more free radicals (which in turn

can produce further condensation) and x moles of methane, ethane, etc. Then the graphitizability of the char should increase with the number of moles of gas released n_r , where $n_r = \frac{n}{2} + x$, for every mole of reactant converted. Molecules of reactant converted are related to moles of reactant charged, n_c , by the kinetic rate constant or by the equilibrium constant of the reaction. It seems plausible, therefore, that graphitizability should increase with n_r/n_c .

In Fig. 5 most of the mixtures containing biphenyl fall on a straight line relating interlayer spacing to gas generation. Pure phenanthrene and pure anthracene released more gas producing an inflection. This was perhaps caused by $n = 3$ or 4 and more extensive condensation taking place.

Union Carbide tabulated gas generation and interlayer spacings for 21 experiments (for 3000° carbon),⁶ but only six of their experiments show the above relationship (*o*-terphenyl, *p*-terphenyl, hydrogenated terphenyls, dibenzothiophene, 9, 9-bifluorene, and fluorene). Six experiments are reported to have had 'known gas leakage'. The remaining nine points will unexplainedly fall far to the left side of the curve in Fig. 5.

Conclusions

The systems have shown themselves to be ideal for fundamental studies in the mechanism of graphitisation. It is now possible to prepare graphite in any desired degree of graphitisation from known starting materials free of catalytic impurities.

Broad decreases in graphitizability were exhibited in both systems as the biphenyl content was increased. This was demonstrated in the 2800° carbons by increases in interlayer spacing and electrical resistivity, as well as by decreases in crystallite height, relative crystalline orientation, and helium density. Therefore, the addition of small amounts of biphenyl or similar compounds to the refinery heavy fuel oil before the thermal cracking step should produce petroleum coke of controllable isotropy for nuclear graphite. Likewise the removal of biphenyl or similar aromatic, non-planar compounds or their precursors, such as benzene, from the heavy fuel oil may improve the graphitizability of the coke.

A triple-phase separation was observed in cokes from the anthracene-biphenyl system and not in the phenanthrene-biphenyl system. This was presumably brought about by the much greater reaction rate of anthracene during carbonisation compared to that of biphenyl. Probably as a result of the phase separation and the Cornuault effect,²⁰ the two systems were not equally affected by equal concentrations of biphenyl. The anthracene-biphenyl system always maintained a much higher degree of graphitizability than did the phenan-

threne-biphenyl system. The 2800° carbons from the latter system were disordered at even a 5% biphenyl concentration.

A relationship between the quantity of gas generated during carbonisation and the degree of graphitisation later attained exists. This suggests a quality control technique applicable to the refinery or to the coke oven. A small sample can be carbonised and the pressure developed after the reaction is complete may serve as an index of ultimate graphitizability, if the system is well-defined. This should assist the refinery in adjusting processing conditions. Similarly, coal tar pitch can be checked for graphitizability without the necessity of forming, baking and graphitising a test piece.

The important role of kinetics on the carbonisation process and the effect on graphitizability had been indicated and deserves further study.

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DISCUSSION

Dr. F. L. Shea (Great Lakes Research Corp., Elizabethton, Tennessee, U.S.A.):—Have measurements been made concerning the effect of pressure on the yield of carbon from anthracene?

Author's reply:—We now have studies underway to look at the effect of carbonisation pressure on the yield of coke and, subsequently, graphite produced. It is, of course, generally recognised that carbonisation under

pressure does enhance yield and we fully expect to find this to be the case.

A. L. Hardstaff (British Acheson Electrodes Ltd., Sheffield):—You have presented an interesting concept in raw materials for the manufacturers. In the nuclear field it would be very useful for the graphite manufacturer to have access to a raw material in which the isotropy can be varied. What is the long-term future for the processes described in your paper?

Author's reply:—When we carbonise under high pressures (up to 38,000 lb/in²) we do find that the

morphology of the coke and, indeed, the graphite subsequently produced is markedly affected. Carbonisation of anthracene, for example, at elevated pressures can result in a botryoidal structure instead of a needle-like structure produced by carbonisation at about 1000 lb/in², as used in this paper. It is difficult to assess the long-term commercial future of high-pressure carbonisation since it will obviously be more expensive. On the other hand, enhanced yield of carbon and the ability to produce a more graphitisable coke (as can be done in some cases) can perhaps offset the increased expense.