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THE IMPORTANCE OF CARBONIZATION CONDITIONS ON THE CHARACTER OF PHENANTHRENE COKE AND ITS GRAPHITIZABILITY

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Abstract—The coking of liquid phenanthrene in a batch reactor was followed by measuring the formation of pyridine insolubles as a function of time over the temperature range 510–570°C. Following an induction period, the disappearance of pyridine solubles is first order, with the rate constants having an activation energy of 65 kcal/mole. This is significantly higher than the activation energy (46 kcal/mole) associated with the rate constants describing the carbonization of the isomer, anthracene. As the rate of carbonization increases, the low-temperature cokes produced decrease in their subsequent graphitizabilities. Further, the reactivity to air of the graphitized carbons is increased.

Key Words—Phenanthrene, pyridene solubles, carbonization, graphitization.

1. INTRODUCTION

Brooks and Taylor, in their seminal studies of some years ago, showed that during the carbonization of graphitic precursors like coal-tar pitches, an intermediate phase or mesophase is formed[1]. This intermediate phase is composed of isochromatic areas that increase in size and magnitude at the expense of the original isotropic liquid phase, as carbonization proceeds. More recently Rouzaud and Oberlin, using optical microscopy and transmission electron microscopy, show that in the first stage of carbonization, elemental, basic structural units are associated edge-to-edge and face-to-face in parallel areas exhibiting local molecular orientation[2]. The basic structural units can be <1 nm in size. The extent of the local molecular orientation attained, prior to the fluidity of the medium decreasing to too low a value, is the primary factor determining subsequent graphitizability. As Rouzaud and Oberlin say, "The game is over" at this point, in so far as how graphitizable the material will be.

Mochida and co-workers note that the carbonization reaction proceeds through radical initiation, propagation, recombination (condensation), and termination[3]. They conclude that at too high a carbonization temperature (or too high a carbonization rate), all of these processes take place too rapidly. They also conclude that there is little time for growth of an extended isochromatic area (or areas of large molecular orientation, according to Rouzaud and Oberlin) prior to fluidity of the medium becoming too low. Thus, it is important to have information on coking rates of aromatic compounds that are major constituents of important commercial feedstocks.

This paper is concerned with the carbonization rates of phenanthrene, an important non-linear aromatic compound that is found in coal-tar pitch feedstocks. In particular, the effect of carbonization temperature (or rate) on the graphitizability of the coke produced is studied.

2. EXPERIMENTAL

2.1 *Reactants*

Phenanthrene, used in most of the research, was obtained from Aldrich Chemical Company without further purification. It had a specified purity of >98% and a melting point of 99–101°C. A limited amount of a higher purity phenanthrene (>99%) was available from Eastman Kodak Company. The higher purity phenanthrene gave basically the same results on carbonization as the lower purity material. Some of the properties of phenanthrene are summarized in Table 1.

2.2 *Carbonization*

2.2.1 *Equipment and coking procedures.* The batch tubing reactors used were identical to those described in the preceding paper[4]. Each reactor was evacuated to <30 Pa pressure prior to the start of a run. Scaroni, *et al.*[4] showed that the addition of N_2 (6.9 MPa at carbonization temperature) did not significantly affect the carbonization rate of anthracene, compared to runs where carbonization was performed in a system initially under vacuum. Consequently, most of the phenanthrene carbonizations were done in a system initially under vacuum. As

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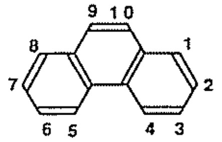
Table 1. Structural formula and numbering scheme



Phenanthrene

Empirical formula	$C_{14}H_{10}$
Molecular wt, g/mol	178.2
Melting Point, °C	100
Normal boiling point, °C	340
Origin	Coal tar contains ~4.0%
Family	Structural isomer of anthracene
Geometry	Flat

described previously[4], carbonization runs were performed by immersing the tubular reactors into a heated, fluidized sand bath. Quenching of the reactors, following a run, was accomplished by lifting them from the bath and quickly immersing them in water. Complete procedures are described elsewhere[5].

2.2.2 *Product analyses.* For the purposes of this investigation, coke was defined arbitrarily as pyridine-insoluble (PI) material. A complete description of the procedure used to determine PI is given elsewhere[4,5].

The composition of the product gases from the coking of phenanthrene was measured quantitatively by gas chromatography, as described elsewhere[4]. Gel-permeation chromatography (GPC) was used to measure molecular weight distributions in PI fractions, also as described elsewhere[4].

2.2.3 *Calcining of low temperature coke.* Calcination was performed at 1200°C in a tube furnace. Approximately 4-g samples were placed in graphite crucibles with lids. The crucibles were placed in a 5.5-cm diameter quartz tube. Nitrogen was passed through the tube. Samples were heated to calcination temperature at a rate of 10°C/min and held at maximum temperature for 1 h. Calcination yielded sample weight losses ranging between 10–20%, depending upon the PI content of the low temperature coke.

The level of PI in the sample to be calcined was an important parameter in influencing the state of the product. For samples containing around 40% PI, calcination resulted in sample agglomeration and swelling. The resulting calcined coke button occupied two to three times the original volume. Samples with 80% or greater PI showed no particle agglomeration and slight shrinkage.

2.2.4 *Graphitization of the calcined cokes.* Calcined material was ground in an agate mortar and pestle until it all passed through a 325 (44 μm) sieve. A graphite-resistance furnace was used for graphitization. Samples of 1-g weight were placed in graphite crucibles and loaded into the furnace. A stream of Ar flowed through the furnace during heat treatment. Heat-up rate was approximately 20–30°C/min, with a soak time of 1 h at maximum temperature.

2.2.5 *X-ray diffraction measurements.* X-ray diffraction measurements were made on the 1200°C and 2500°C carbons, using procedures previously described[6,7]. Measurements were made on –325 mesh calcined cokes and graphites. Silicon was used as an internal standard. Interlayer spacings, d, and average crystallite height, L_c, were measured from the (002) peaks. The average crystallite diameter, L_a, was estimated using a correlation with interlayer spacing[8].

$$d = 3.354 + 9.5/L_a \qquad (1)$$

Intensity of the (002) X-ray diffraction peak is expressed as the area under the peak above background levels. This area was divided by the integrated area of the adjacent silicon reference peak. In this way, all data were placed on a common basis for comparative purposes.

2.2.6 *Reactivity measurements.* Reactivity of calcined cokes and graphitized carbons to 0.1 MPa air was conducted in a thermogravimetric analysis apparatus. Carbon burn-off as a function of time was measured over a wide range of burn-off. Samples of –325 mesh material were used for this measurement.

2.2.7 *Surface areas.* Surface areas of –325 meash calcined cokes and graphitized carbons were measured using the standard BET method and Kr as the adsorbent at –196°C.

3. RESULTS AND DISCUSSION

3.1 *General considerations*

Studies of the carbonization of organic substances in batch reactors requires an understanding of the state of the material contained in this system. Lewis and Edstrom[9] studied the thermal reactivity of a series of aromatic hydrocarbons using differential thermal analysis. The aromatic compounds were classified as thermally unreactive if no carbonaceous residues were observed at 750°C at atmospheric pressure. Phenanthrene was found to be sufficiently stable under these conditions, that negligible condensation reactions occurred prior to complete volatilization. It was found that hydrocarbons with ionization potentials greater than 7.0 ev were unreactive under these conditions.

The temperature range used in most of this study for the carbonization of phenanthrene was from 510°C–570°C. This is to be compared with the critical temperature (T_c) of phenanthrene of 605°C. Phenanthrene can, therefore, be expected to partition into the vapor and liquid phases before significant condensation (chemical) reactions occur. The amount of materials in the vapor will be determined by the vapor pressure and the reactor volume. Data and calculations necessary to determine the partitioning of phenanthrene between the liquid and vapor states under the carbonization conditions used in this research are fully considered elsewhere[4,5]. The percentage of phenanthrene in the vapor phase as a function of the carbonizing temperature ranged from 4.5% at 510°C to 5.5% at 570°C for a 5 g charge to the reactor.

Work by Madison and Roberts[10] showed that the batch pyrolysis of anthracene vapor at 500°C for 90 min resulted in little conversion. By contrast, liquid-phase pyrolysis of anthracene under the same conditions showed high levels of conversion to a heavy residue. Differences between gas and liquid-phase pyrolysis rates were primarily attributed to the approximately 50-fold greater concentration of the organic in the liquid phase than in the vapor phase. A two-phase system was apparent in the material removed from the batch reactor following phenanthrene carbonization at temperatures between 510°C and 570°C. Vapor-phase material was relatively light colored and was essentially completely soluble in pyridine, suggesting the presence primarily of low-molecular-weight constituents. The vapor-phase material coated the inside of the reactor and covered the darker residue that resulted from liquid-phase pyrolysis. The carbonization experiment performed above the critical temperature did not, as expected, show a two-phase system.

The effect of sample size charged to the batch reactor on carbonization kinetics (yield) was investigated. Carbonizations were carried out at 550°C for 2 h, and pyridine extractions were performed on the resulting solid material. Yields of PI material as a function of weight of phenanthrene charged to the reactor are presented in Fig. 1. Also shown in Fig. 1 are yields based upon starting weight of phenanthrene in the liquid phase. A sample size of 5 g or more gave sufficient amounts of carbonaceous material derived from the liquid phase to provide a reproducible measure of PI upon extraction. The reproducibility of the pyridine extractions was ±1%. It was also important to produce sufficient material for characterization and further heat treatments. Small sample charges naturally contained a higher proportion of vapor-phase material. This resulted in errors due to problems of obtaining a representative sample for extraction and increased significance of errors in estimating vapor phase material from available theoretical equations. Based upon these results, a sample size of 5 g was used in subsequent carbonization experiments.

Agitation of the reactors (350 cycles/min) was provided in order to eliminate possible mass transfer control of carbonization rates. As expected, agitation resulted in more rapid heat-up of the reactor to the desired temperature. However, there appeared to be no significant effect of agitation on pyridine insolubility of the carbonized liquid phase material, when allowance was made for the difference in heat-up time to reaction temperature.

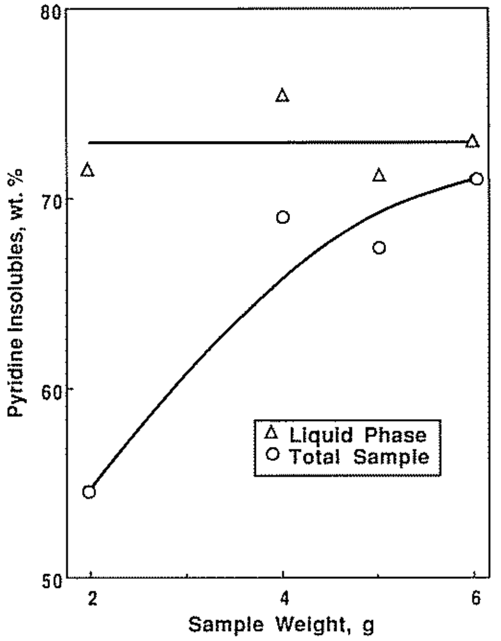


Fig. 1. Effect of sample weight on the conversion of phenanthrene into PI: 550°C, 2 h.

3.2 *Gas formation during carbonization*

Analysis of the gas was made using chromatography, following carbonization at 550°C for 105 min. About 50% PI was formed under these conditions. Results of the analysis are shown in Table 2. The amount of methane measured was considerably higher than that of H_2. The ratio was roughly 3 to 1. This is to be compared with the ratio of methane to H_2 produced during the carbonization of anthracene, that is 0.5. This indicates that hydrogenolysis is a more important reaction during phenanthrene carbonization than during anthracene carbonization. As found for anthracene carbonization[4], the ratio of the moles of gas produced to the moles of phenanthrene converted to PI was small.

Union Carbide[11] reported, from studies of the thermal polymerization of naphthalene, that some partially hydrogenated aromatic compounds are formed during carbonization. They carbonized naphthalene at 500°C for different time intervals ranging from 4 h to 25 h. The 4 h sample gave a gas mixture consisting of 91% H_2, whereas, for a 25 h

Table 2. Analysis of gas from selected carbonization run, phenanthrene at 550°C for 105 min initially under vacuum

Gas	Volume, %
CH_4	68.0
H_2	22.8
C_2H_6	9.2

carbonization, only 12% H_2 and 64% methane were detected. It appeared more probable that the generation of CH_4, C_2H_6, and C_3H_8 came about from the thermal cracking of partially hydrogenated species, rather than by the rupturing of carbon-carbon bonds in fully aromatic molecules. The high levels of low-molecular-weight hydrocarbons observed in the carbonization of phenanthrene could have arisen by a similar means.

3.3 *Rates of carbonization*

The kinetics of phenanthrene carbonization were followed by measuring the development of PI over time at a particular temperature. These experimental results at four different temperatures are shown in Fig. 2. A finite amount of time is required for the appearance of PI. This time interval has been referred to as the induction period (t_i). From an examination of Fig. 2 it is seen that the t_i period decreases with increasing temperature. An induction period is the result of measuring the progress of the carbonization by a solvent-extraction technique. Thermal reactions of phenanthrene are taking place during the induction period; however, the early products of carbonization are soluble in pyridine. Beyond the induction period, the solid product becomes progressively more insoluble in pyridine.

Two methods were employed for the analysis of kinetic data. One is based upon the rate constant, k, obtained from a first-order plot of disappearance of pyridine solubles (PS) versus time. The measured PI were calculated on the basis of material in the liquid phase by computing a ratio of wt% PI/wt% PI_{max}, where wt% PI_{max} is the wt% of PS initially contained in the liquid phase. The amount of PS material is therefore 1–wt% PI/wt% PI_{max}. This calculation correctly assumes that the weight of gas produced during carbonization is negligible. It also assumes that carbonization of phenanthrene in the vapor state is slow (negligible) compared to the carbonization rate of liquid phenanthrene. The rate of disappearance of PS can be expressed in differential form.

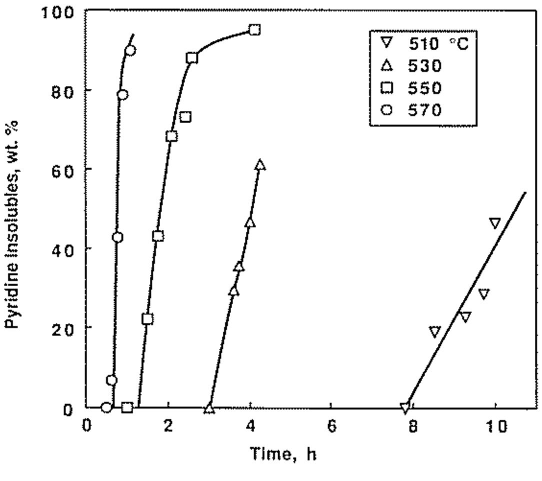


Fig. 2. PI measured as a function of time for various carbonization temperatures.

$$k = \frac{-d \ln\left(1-\dfrac{\text{wt\% PI}}{\text{wt\% PI}_{\max}}\right)}{dt} \tag{2}$$

If the disappearance of PS in first order, the derivative will equal a constant or the reaction-rate constant. Integration of equation (2) gives the standard first-order kinetic expression in terms of the disappearance of PS:

$$1-\frac{\text{wt\% PI}}{\text{wt\% PI}_{\max}} = \exp(-kt) \tag{3}$$

A plot of ln (1–(wt% PI/wt% PI_{max})) versus time will give a straight line of slope–k in the case of first-order kinetics. Such a plot was prepared from the data collected over the temperature range from 510°C to 570°C and is shown in Fig. 3. The data at 570°C show a rapid rate of reaction as is evident from its large slope. The data at 510°C tended to be scattered somewhat, probably due to difficulties in maintaining proper reaction conditions over such a long induction period. Values for the induction period are given in Table 3.

A least-squares analysis of the data in Fig. 3 was made in order to obtain a best-fit line and its associated slope. A correlation coefficient was computed to indicate the suitability of the fit. Values of rate constants and correlation coefficients are presented in Table 4. The carbonization and extraction data from experiments at 530°C to 570°C gave correlation coefficients suggesting first-order kinetic behavior.

An Arrhenius plot for the rate constant, k, is presented in Fig. 4. The results for anthracene carbonization are also presented. The activation energy determined from the plot is 65 kcal/mole with a correlation coefficient of 0.965. The corresponding pre-exponential factor was 2.4×10^{17} h^{-1}. The rate constant for the disappearance of PS with time can be compared to that reported by Scaroni, *et al.*[4] for the carbonization of anthracene, 1.4×10^{13} exp (–46 kcal/mole/RT) h^{-1}. The activation energy for anthracene carbonization was considerably lower than that determined for phenanthrene carbonization. The pre-exponential term is larger in the case of phenanthrene than the corresponding value for anthracene carbonization, thus exhibiting the usual compensation effect[12]. The overall result is that phenanthrene carbonizes much more slowly than does anthracene over the temperature range of importance in liquid-phase coking.

In the second method of analyzing the kinetic data, the induction period (t_i) is utilized. As discussed in the preceding paper[4], the induction time can be roughly related to the time required for reduction of the concentration of reactant to a fraction of its initial value. As reasoned previously[4], the Arrhenius plot of ln(t_i) versus ($1/T$) should yield a

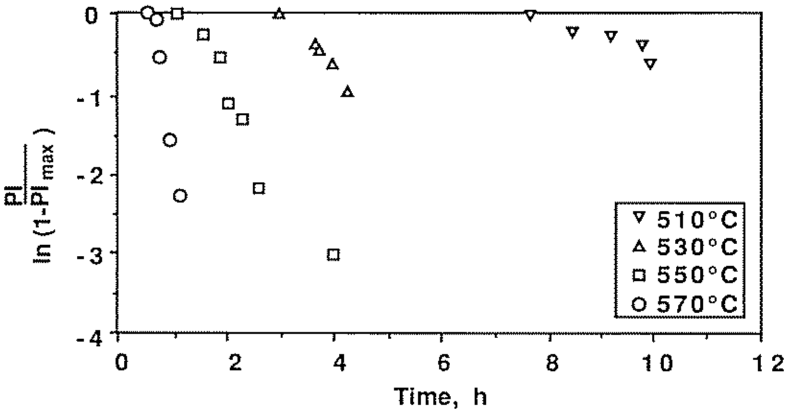


Fig. 3. First order plots of the carbonization of phenanthrene as measured by PI.

straight line, from which an activation energy can be determined. Such a plot is presented in Fig. 5. A linear least-squares analysis gives an activation energy of 54 kcal/mole with a correlation coefficient for the fit of 0.999.

Figure 5 also includes results from Scaroni, *et al.*[4] on induction periods for the carbonization of anthracene. The rates of formation of PI from anthracene and phenanthrene were much different once their formation began. There is also a major difference in the times for the first appearance of PI when starting with these different precursors. It suggests that initial reactions in the carbonization sequence involving anthracene proceed at a faster rate than initial reactions involving phenanthrene. At later stages of carbonization, when reacting species have reached a larger size through free-radical and condensation reactions, reactions resulting in further increase in size (and production of additional PI) have different rates that still show dependency on the starting precursor.

3.4 *Permeation chromatography studies on PI*

Gel-permeation chromatography was used to investigate the molecular weight distribution of a representative sample from the coking of phenanthrene. The sample analyzed by GPC was the PI fraction generated following carbonization of phenanthrene at 550°C for 105 min; it had a PI of 39%. Sample preparation for GPC and calibration procedures were described previously[4]. The GPC analysis results are presented in Fig. 6. This figure represents the molecular-weight distribution expressed on a relative basis. The lower limit of the molecular weight distribution suggests the presence of dimeric phenanthrene at a weight of 356. Some of the structure observable in the molecular-weight distribution for molecular weights under 1000 was most likely the result of a preponderance of molecular weights that are multiples of the monomer, phenanthrene. This would be consistent with the polymerization/condensation reaction scheme. From a cumulative distribution curve, the number average molecular weight was determined to be 1280.

A proton NMR spectrum was used to measure the degree of hydrogenation of the PI when reduced by lithium in ethylenediamine. The NMR spectrum was obtained using $DCCl_3$ as the solvent, and is shown in Fig. 7. Tetramethylsilane was used as the internal reference for measuring chemical shift. One peak occurred at 7.2 ppm and was associated with aromatic protons, Ar—H. A cluster of three peaks occurred at 1.7 ppm, 1.3 ppm, and 0.9 ppm. The 1.7-ppm peak may be associated with an allylic proton, $C{=}C{-}CH_3$. The 1.3-ppm and 0.89-ppm peaks are related to secondary R_2CH_2 and primary protons, $R{-}CH_3$, respectively. The detection of primary protons and allylic protons indicates that cracking of the phenanthrene had opened up some of the rings, since only secondary protons would normally be expected in the case of undisrupted rings. The relative size of the 7.2-ppm peak to the three other observed peaks indicates that the reduction procedure was successful. The amount of aromatic hydrogens remaining in the reduced PI was, therefore, small as compared to hydrogens associated with non-aromatic systems.

Table 3. Induction periods for appearance of PI

Temperature, °C	Induction Time, h
510	7.8
530	3.0
550	1.3
570	0.62

Table 4. Rate constants for phenanthrene carbonization

T, °C	k, h^{-1}	Correlation Coefficient
510	0.20	0.826
530	0.73	0.953
550	1.14	0.940
570	4.27	0.940

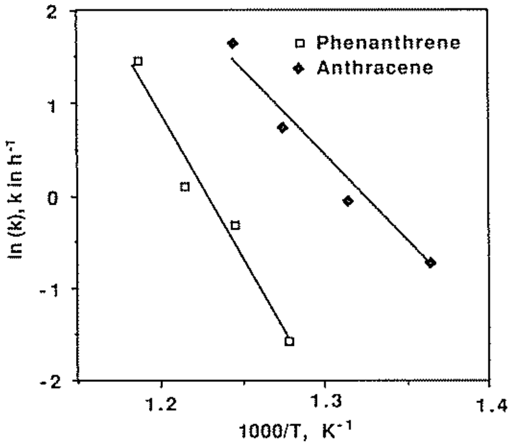


Fig. 4. Arrhenius plots for the formation of PI: ○ phenanthrene, △ anthracene[4].

3.5 *Calcination and graphitization*

The calcination stage was carried out at a 1200°C soak temperature and a soak time of 1 h. In one set of experiments, samples of low temperature (green) coke were not pyridine-extracted prior to calcination. During calcination, volatiles were released from the sample. These volatiles tended to deposit as a white-to-yellowish material at the cool effluent end of the tube furnace. Since these samples contained about the same level of PI (~90%) when extracted, the amount of volatiles released during calcination was approximately the same for all samples. A series of green coke samples which were extracted to a PI level of ~40% were also calcined.

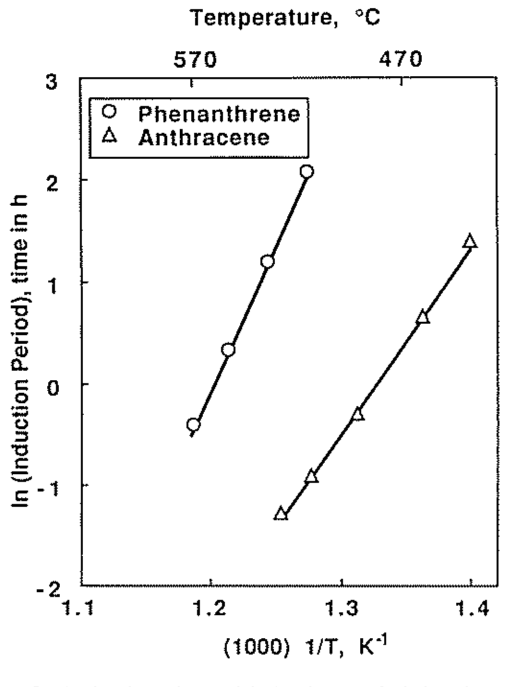


Fig. 5. Arrhenius plots of induction period for the appearance of PI: ○ phenanthrene, △ anthracene[4].

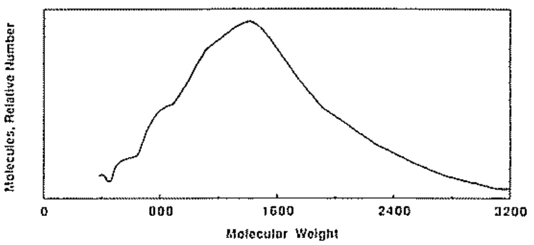


Fig. 6. Gel permeation chromatography molecular weight distribution of reduced PI from the carbonization of phenanthrene: 550°C, 105 min.

The samples passed through a fluid phase and puffed up to several times their original sample volume.

Visual observation of the calcined cokes revealed some differences that appeared to be related to the temperature that was used to produce the green coke. The calcined coke produced from green coke initially carbonized at 510°C to a PI content of ~90% had an almost metallic luster. By contrast, calcined coke produced from green cokes carbonized at higher temperatures (530–570°C) had a dull luster. Differences in appearance are probably the result of differences in crystallite alignment. Better alignment would result in the surface having a higher reflectance or luster. Material carbonized above the critical temperature of phenanthrene at 630°C appeared to be glassy and tended to be more porous than those solids formed below the critical temperature.

Another physical observation made on the calcined cokes was the differences in their grindability. Calcined cokes produced from phenanthrene carbonized at 510°C were noticeably easier to grind to –325 mesh material in an agate mortar and pestle, than those produced from 570°C green coke. Differences in coke grindability have been attributed to differences in crystallite alignment by Walker, *et al.*[13]. Cokes with the highest crystallite alignment were generally the easiest to grind.

The data for the 1200°C cokes and 2500°C carbons are shown in Tables 5 and 6. The first four samples in Table 5 were produced from green cokes having PI of greater than 90%. The latter three samples were produced from PI, which represented about 40% of the total material produced during low-temperature carbonization. Relative X-ray intensity data for the calcined samples are presented in Fig. 8. As carbonization temperature (rate) is increased, the relative X-ray intensity of the (002) diffraction peak for the calcined cokes descreases. As discussed previously[7], relative X-ray intensity of the (002) diffraction peak can be used as a measure of relative crystallite alignment in the carbons being studied. The greater the peak intensity, the greater the degree of crystallite alignment. A greater degree of crystallite alignment in calcined cokes is expected to be derived from greater degrees of local molecular orientation achieved during the carbonization process. Indeed, optical microscopy studies using po-

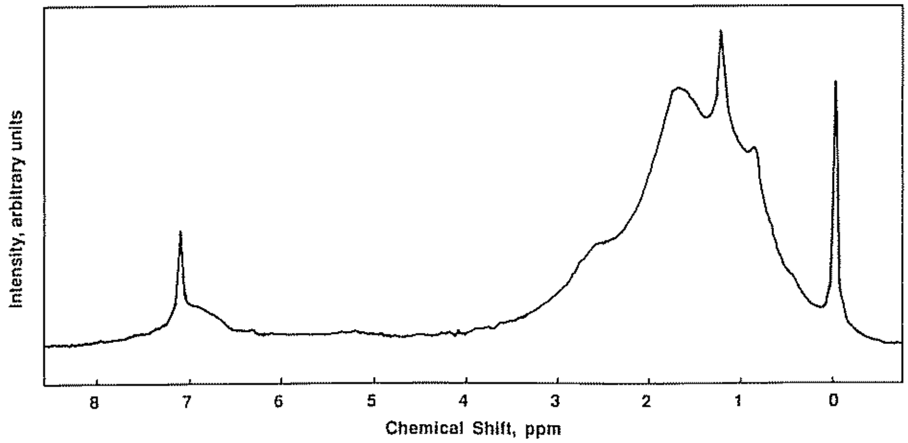


Fig. 7. Nuclear magnetic spectrum of reduced PI obtained from the carbonization of phenanthrene: 550°C, 105 min.

larized light, confirmed this thought[5]. That is, the average size of mesophase spheres formed during carbonization, and the extent of isochromatic areas, clearly increased as carbonization temperature decreased for equivalent extents of PI formation. For the samples produced at 510°C and 570°C by carbonizing for 1440 min and 60 min, respectively, to yield >90% PI, isochromatic areas extended over ~75 μm and ~14 μm, respectively.

Results for the calcined coke produced from the green coke formed above the T_c of phenanthrene are interesting. Even though the rate of formation of PI at 630°C in the vapor phase was much less than the rates of formation of PI in the liquid phase below the critical temperature, the calcined coke exhibits negligible crystallite alignment. Carbonization in the vapor phase was slow since the concentration of reactant was much less than that existing in the liquid phase, as previously discussed. But perhaps more important, the lack of close approach of the vapor molecules resulted in negligible van der Waals attraction between them and a consequent failure, then, of elemental, basic structural units to associate edge-to-edge or face-to-face in parallel.

Table 6 and Figs. 8–10 present X-ray diffraction results for the graphitized samples. As seen in Fig. 8, the correlation between relative crystallite alignment and carbonization temperature of phenanthrene continues to hold for the graphites. This emphasizes the point made by Rouzaud and Oberlin[2] that the "game is over" in determining potential crystallite growth during carbonization at very low temperatures. Figures 9 and 10 emphasize the strong effects of carbonization temperature on L_c and d-spacing of the graphitized samples. As discussed by Franklin[14], as the interlayer (d) spacing decreases, the fraction of basal planes within the crystallite exhibiting registry in an abab alignment increases. The carbon produced from the green coke formed above T_c was completely turbostratic, having an interlayer spacing above 0.344 nm [14].

Table 5. X-ray measurements on calcined cokes

Carbonization Temperature, °C	(002) Peak Height, Counts/s	$I_{(002)}/I_{Si}$
510	187	2.12
550	62	0.82
570	55	0.51
630	nil	nil
530	100	—
550	70	—
570	60	—

3.6 *Reactivities in air*

Table 7 summarizes reactivity results. Reactivities are expressed as maximum reaction rates normalized to per-unit starting weight. As can be seen in Fig. 11, the maximum rates occurred close to zero percent carbon burn-off. It is seen in Table 7 and Fig. 11 that reactivities of both the calcined cokes and graphites increase as carbonization temperature is increased. Note further that reactivities sharply decrease as the calcined cokes are taken to graphitization temperature. Assuming an activation energy of 44 kcal/mole for the carbon-air reaction[15], coke reactivities at 670°C are estimated to be 25 times greater than graphite reactivities. Accompanying the changes in reactivity are changes in specific surface areas of the samples. As crystallite alignment and crystallite size in the samples improves, specfic surface areas would be expected to decrease. Reactivities have also been normalized to the specific surface areas prior to carbon gasification. As expected[15], total surface areas are not successful in normalizing reactivity results.

3.7 *Thoughts on carbonization*

Clearly, carbonization temperature has been shown to be an important variable in determining the subsequent graphitizability of cokes produced

Table 6. X-ray measurements on graphitized carbons

Carbonization Temperature, °C	(002) Peak Height Counts/s	$I_{(002)}/I_{Si}$	*d*,nm ± .0001	L_c,nm	L_a,nm
510	9100	6.87	0.3363	130	106
550	2800	2.82	0.3366	113	79
570	2100	2.23	0.3373	83	50
630	584	1.86	0.3452	11	10

from phenanthrene. As discussed previously, enhanced graphitizability correlates with increased isochromatic areas seen in the low-temperature cokes. Two main processes are involved in carbonization when areas of measurable molecular orientation are produced—one is physical and the other is chemical. The chemical process involves radical initiation in the reactant and radical recombination (condensation) to larger molecular species. During carbonization, these molecular species existing in the liquid phase diffuse and mix at some rate. This is the physical process. If they are planar and sufficiently large in diameter, they will align if they come in close enough proximity to each other due to van der Waals attraction. That is, they will exhibit molecular orientation. Mochida and co-workers recognize, however[3], that if the chemical process is too rapid, molecular growth in turn occurs too quickly, resulting in a rapid reduction in the rate of mixing (diffusion) of the molecules. They simply do not have time to align before molecular diffusion rates become too low.

In this context, it is at first tempting to attribute the effect of carbonization temperature of phenanthrene on its subsequent graphitizability to this phenomenon. With increasing carbonization temperature from 510 to 570°C, carbonization rates increase sharply (activation energy of ~65 kcal/mole), thereby reducing the time for molecular alignment to be achieved. However, there are a number of arguments which appear to work against this hypothesis.

1. First, measurements have been made on the viscosity (η) of a predominantly anisotropic mesophase pitch which exhibits pseudo-Newtonian behavior[16]. Viscosity dependence on temperature (T) is quite strong, that is, η is proportional to exp (43 kcal/mole/RT). It is estimated that the pitch η at 570°C is 6.7 cp. Knowing the viscosity of the liquid, one is able to estimate the self-diffusion coefficient (D_s) of the molecules constituting the liquid using the approach of Dullien[17]. In this case, for a η = 6.7 cp, D_s is estimated as 10^{-6} cm²/s. Having D_s it is now possible to estimate over what distance diffusion will occur during the time involved in a carbonization run. For example, carbonization of phenanthrene at 570°C to produce ~90% PI required ~1 h. Using the Einstein equation

$$d^2 = (D_s)(t) \tag{4}$$

it is estimated that the diffusion distance (d) for a diffusion time of 1 h will be ~840 μm. As discussed previously, the isochromatic areas present in the

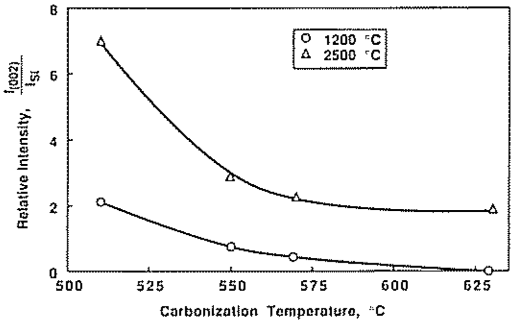


Fig. 8. Relative intensity of (002) X-ray diffraction peak for calcined and graphitized samples plotted as a function of carbonization temperature.

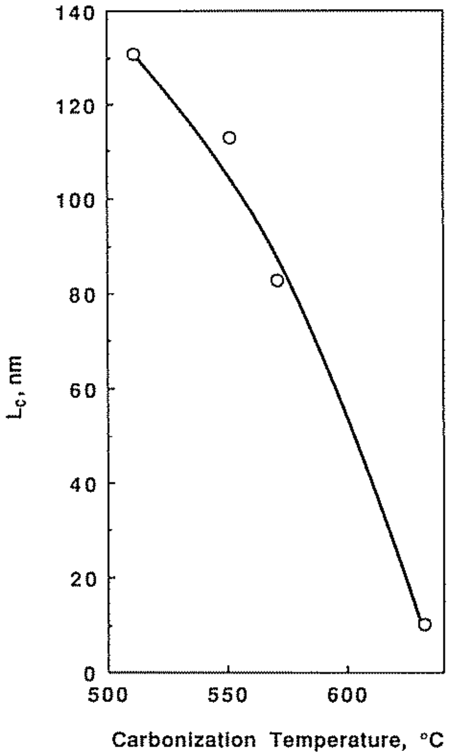


Fig. 9. Change in average crystallite height of graphitized carbon with carbonization temperature.

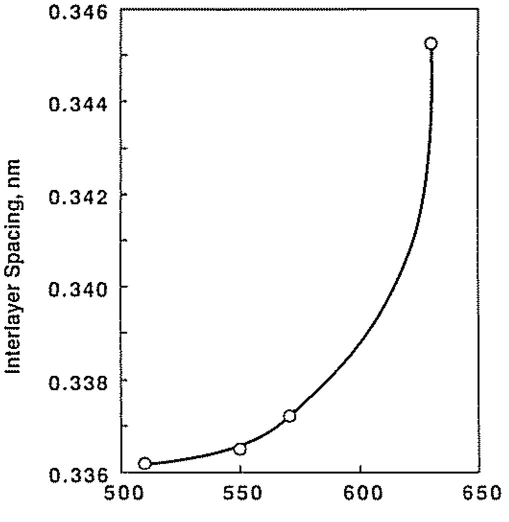


Fig. 10. Interlayer spacing of graphitized carbons plotted as a function of carbonization temperature.

~90% PI coke produced upon carbonization of phenanthrene at 570°C for 1 h approximate 14 μm in size. It is thought, then, that diffusion rates (and diffusion distances) during carbonization at 570°C are sufficient to minimize the effect of mass transport resistance on limiting molecular orientation.

2. Second, some years ago, Walker and Weinstein[18] studied the graphitizability of low-temperature cokes produced from anthracene and phenanthrene at 550°C, using a hold time of 12 h in order to assure a very high yield (>90%) of PI. The coke produced from anthracene was more graphitizable than that produced from phenanthrene, despite the fact that the carbonization rate of anthracene is estimated to be about five times greater than that of phenanthrene under these conditions. In other words, it is concluded that an increase in carbonization rate did not result in a decrease in extent of molecular alignment during carbonization.

3. Third, preparation of low-temperature cokes from phenanthrene at 570°C was performed in reactors which were both agitated and not agitated, in this study. From X-ray diffraction measurements, no detectable differences in graphitizability of the cokes produced was observed[5]. In other words, enhancement of bulk mass transport did not improve subsequent graphitizability of the coke produced.

However, there is at least one argument in favor of mass transport explaining the results with phenanthrene; that is, the difference in temperature dependency of carbonization rate for phenanthrene compared to that for anthracene[4,19], acridine[19], and phenazine[19]. The activation energy describing the rate of formation of PI during the carbonization of phenanthrene is 65 kcal/mole. This is to be compared to activation energies ranging from 36 to 46 kcal/mole for the carbonization of the latter three hydrocarbons. Since it has just been estimated that the D_i for molecules in the liquid during carbonization is activated and described by an activation energy of roughly 43 kcal/mole, it means that for phenanthrene carbonization the chemical rate increases more sharply with temperature than does the diffusion rate. Conversely, for anthracene, acridine, and phenazine the chemical rate is estimated to just increase at an equivalent rate to the diffusion rate or, even, more slowly. It is interesting that whereas increasing carbonization temperature has been seen to reduce the subsequent graphitizability of low-temperature coke produced from phenanthrene, carbonization temperature has a negligible effect on graphitizability of cokes for the other three hydrocarbons[4,19].

Let us now consider one possibility, from a chemical perspective, as to why increasing the carbonization temperature of phenanthrene reduces subsequent graphitizability. This has been considered previously[20]. As shown, reactivities of phenanthrene are expected to be different at different positions in the molecule. If upon its carbonization the molecule undergoes dehydrogenation at its most reactive 9, 10 positions and 1, 8 positions to form free radicals, polymerization reactions can eventually lead to larger, planar structures[20]. These structures would be expected to be precursors of graphitizable carbons. However, to the extent that dehydrogenation and free-radical formation were to occur at the less reactive 2 and 3 positions, leading to the formation of biphenanthryls, the development of anisotropic domains in the mesophase would be drastically reduced[20]. These domains could not undergo further intermolecular condensation reactions. Further, the presence of biphenanthryls would lead to their reactions with free radicals formed at the 9, 10 and 1, 8 positions of phenanthrene and thereby again produce less desirable products. Such is thought to have been the case when biphenyl is

Table 7. Reactivity of samples to air

Carbonization Temperature, °C	Reactivity g/g–h	Surface Area m^2/g	Reactivity g/m^2–h
	Calcined Cokes at 570°C		
510	0.134	1.9	0.071
570	0.151	4.1	0.037
	Graphites at 670°C		
510	0.052	1.0	0.052
570	0.130	1.9	0.068

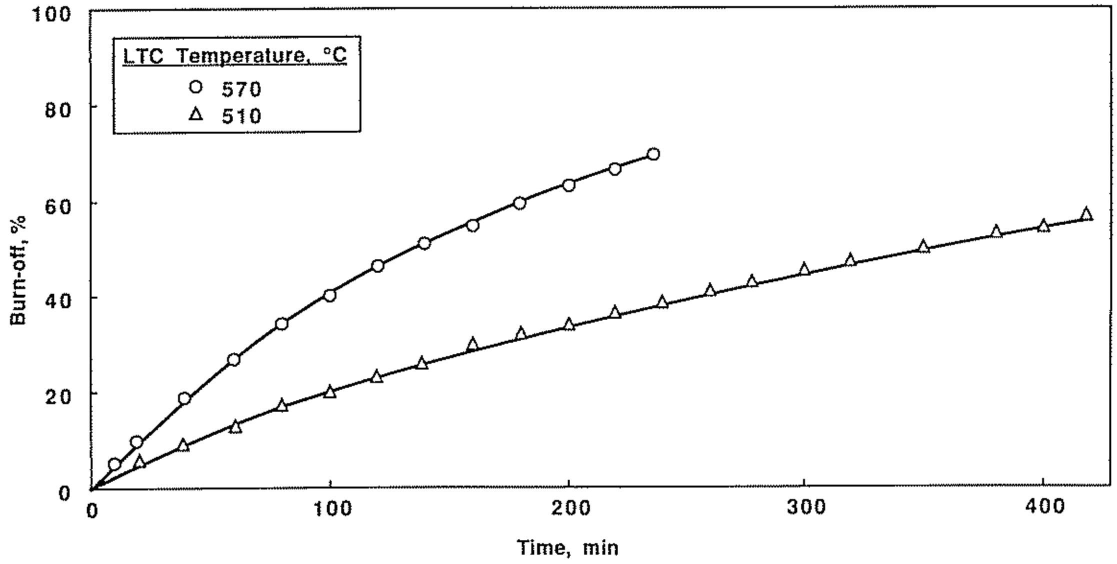


Fig. 11. Reactivity of graphitized carbons in air at 670°C.

mixed with phenanthrene, thereby reducing its graphitizability[21]. Biphenyl exhibits free rotation around its carbon-carbon single bond (as do the biphenanthryls) and thereby reduces the planarity of product molecules with which it reacts. Since the activation energy required to produce free radicals at the 2 and 3 positions in phenanthrene is expected to be higher than that required at the 9, 10 and 1, 8 positions, it is expected that the contribution of the former reactions to the over-all carbonization process would increase with increasing carbonization temperature. This, in turn, should result in the production of a less graphitizable low-temperature coke with increasing carbonization temperature for phenanthrene, as is found.

4. CONCLUSIONS

The carbonization of phenanthrene leads to low-temperature cokes of reasonable graphitizability. However, as carbonization temperature is increased in the range 510 to 570°C, thereby increasing the rate of formation of PI by some 21 times, the graphitizability of the low-temperature cokes is decreased. Possible explanations for this effect appear to exist.

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