

COKES AND GRAPHITES PRODUCED FROM ANTHRACENE, ACRIDINE, AND PHENAZINE

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(Received 31 July 1990; accepted in revised form 14 January 1991)

Abstract—The effect of substitution of nitrogen into the 9 position and 9,10 positions of anthracene in place of C—H groups on the kinetics of carbonization to yield pyridine insolubles (PI) and the properties of the cokes and graphites produced have been studied. Acridine and phenazine exhibit higher carbonization rates than does anthracene. Carbonization of each of these heterocyclics leads to low-temperature cokes exhibiting large flow domain, isochromatic regions and good graphitizability. However, the elimination of nitrogen from the low-temperature cokes upon their calcination does result in the production of cokes and graphites of lower particle densities and higher surface areas. The result is that these carbons have higher reactivities to air and they probably will lead to the production of artifacts of inferior mechanical properties.

Key Words—Coke, graphitization, anthracene, acridine, phenazine.

1. INTRODUCTION

Polynuclear aromatic hydrocarbons vary greatly in their ease of conversion to low-temperature cokes. For example, we have seen that the carbonization rate of anthracene (a planar, linear aromatic) is much more rapid than that of its isomer phenanthrene (a planar, branched aromatic)[1,2]. This difference in carbonization rate has been attributed to the reactivity of the 9 and 10 positions in anthracene being much greater than that at any position in the phenanthrene molecule[3]. Such differences in reactivity are predicted on the basis of known differences in free valence indices (or electron densities) at different positions in the molecules[3].

Reactivities of polynuclear aromatic hydrocarbons are also enhanced by the presence of alkyl chains[4], C—O bonds[5], and nitrogen within the aromatic rings[6]. This study is concerned with the effect of substituting nitrogen in the 9 position and 9,10 positions of anthracene on carbonization rates and the nature of the cokes and graphites produced. The model compounds acridine and phenazine, which are present in coal-tar pitches, are used for this study. Results with these compounds are compared with those obtained for anthracene.

2. EXPERIMENTAL

2.1 Reactants

The aromatics used in this study were obtained from Aldrich Chemical Company at purities >98%. Acridine (C₁₃NH₉) and phenazine (C₁₂N₂H₈) have nitrogen substituted for C—H in the 9 and 9,10 positions in anthracene[1], respectively. Previous

studies with anthracene showed that carbonization rates were the same for this material and anthracene of >99% purity obtained from Eastman Kodak[1].

2.2 Carbonization, calcination, and graphitization

These procedures have been described fully elsewhere[1,2,7]. Consideration was given previously to the effect of weight of charge to the stainless steel tubing reactors (15 cc) on rates of carbonization of anthracene[1]. It was shown that if charges of 4 g or greater were used, sample weight had little effect on results. Thus, a charge of 4 g or greater was used in this study. During carbonization, glass-lined reactors were agitated at 240 cycles/min.

2.3 Measurement of carbonization rate

For the purpose of this investigation, carbonization rate (or rate of low-temperature coke formation) was defined arbitrarily as the rate of formation of pyridine insoluble (PI) material. A complete description of the procedure used to determine PI is given elsewhere[1,7].

2.4 Characterization of products

2.4.1 X-ray diffraction measurements. X-ray diffraction measurements were made on the cokes and graphites using procedures previously described[8,9], with one exception. The intensity of the (002) diffraction peak is given as its height above background instead of area under the peak.

2.4.2 Reactivity studies. Reactivity to air of calcined cokes was measured. The cokes were first ground by hand in a ceramic mortar and pestle to -200 mesh. The reactor used was a tube-furnace described by Taylor[10]. Samples of 2 g were loaded into a ceramic boat and held in the center of a mullite furnace tube. The cokes were heated to 950°C in

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flowing Ar to remove surface oxygen complex prior to conducting gasification in flowing, dried air at 500°C. During gasification, 1-cc samples were taken from the product gas stream and analyzed by gas chromatography. Concentrations of CO and CO₂ were determined and carbon burn-off thus calculated.

2.4.3 *Surface areas.* Surface areas of -200 mesh calcined cokes were measured using the standard BET method[11] and Kr as the adsorbent at -196°C. The apparatus and procedure are described elsewhere[12].

3. RESULTS AND DISCUSSION

3.1 Kinetics of carbonization

Figures 1 and 2 show data for the formation of PI from phenazine and acridine. Figure 3 shows a comparison of rates of formation of PI from anthracene, acridine, and phenazine at 460°C. There are two effects due to the presence of nitrogen in the anthracene ring structure. At a given temperature, the time required for the initial formation of PI decreases. Also, the rate of carbonization once the first PI appears is increased as more nitrogen is contained in the ring structure. It has been suggested previously by Madison and Roberts that replacement of one or more of the C—H groups in anthracene by nitrogen atoms leads to a decrease in the bond dissociation energy of one or more of the remaining C—H bonds[13]. They studied the carbonization of naphthalene and quinoline. It is suggested that this decrease in bond dissociation energy facilitates free radical and condensation/polymerization reactions at the 1,4 and 5,8 positions of acridine and phenazine. The fact that ~90% of the nitrogen originally contained in the starting compounds remains in the low-temperature carbonaceous residues supports the

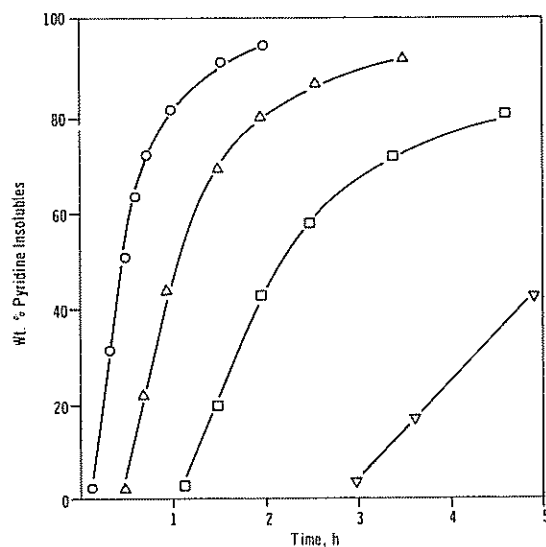


Fig. 1. Effect of time and temperature on the conversion of phenazine into PI: ○ 460, △ 440, □ 420, ▽ 400°C.

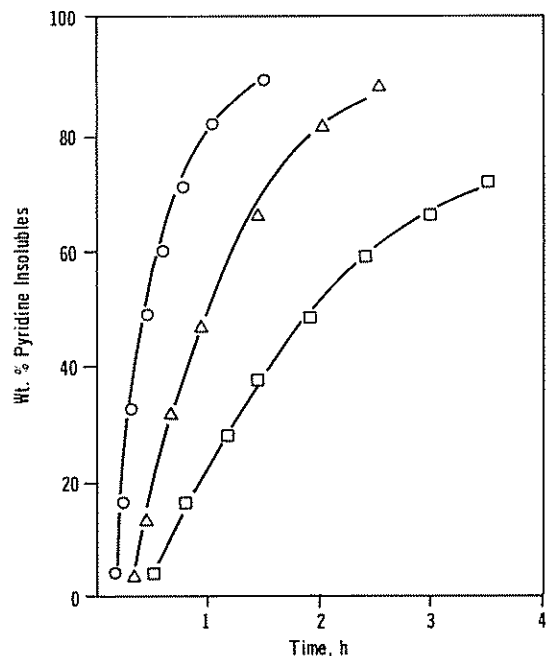


Fig. 2. Effect of time and temperature on the conversion of acridine into PI: ○ 480, △ 460, □ 460, ▽ 440°C.

suggestion that the 1,4 and 5,8 positions are the most likely positions for reactions to occur. This is also in agreement with the hypothesis of Isaacs[14], who studied the carbonization of various heterocyclic nitrogen compounds. By contrast, the 9,10 positions of anthracene are clearly the most reactive for free-radical and condensation/polymerization reactions, as discussed by Scaroni, *et al.*[1], among others.

First-order plots for the disappearance of PS as a function of time for phenazine and acridine are shown in Figs. 4 and 5. Figure 6 presents Arrhenius

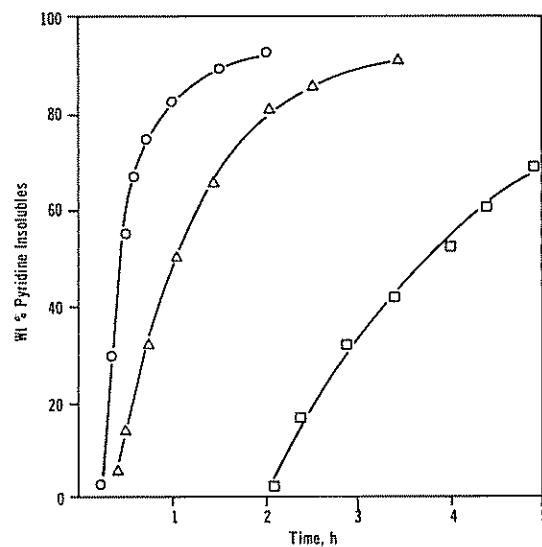


Fig. 3. A comparison of the effects of time and temperature on the conversion of anthracene, acridine, and phenazine into PI at 460°C: □ anthracene, △ acridine, ○ phenazine.

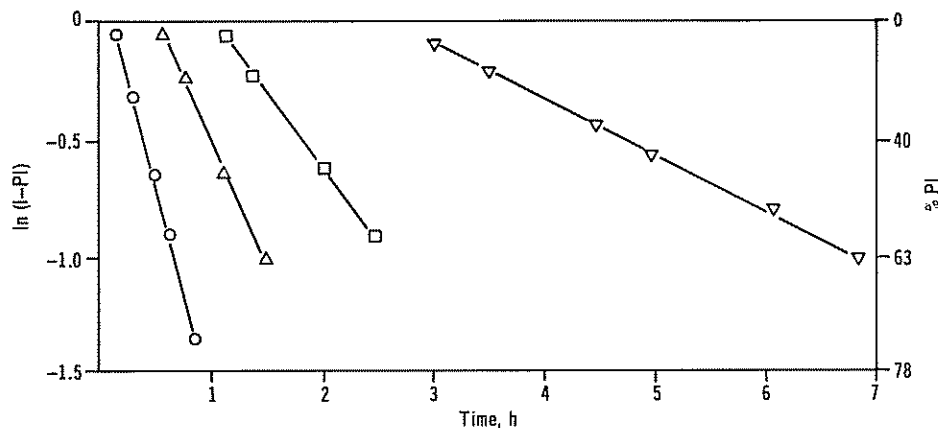


Fig. 4. First-order plots for the formation of PI from phenazine: \circ 460, \triangle 440, \square 420, ∇ 400°C.

plots for the rate constants obtained from the first-order plots, with pre-exponential values and activation energies for the rate constants given in Table 1. The activation energy for the disappearance of PS during carbonization decreases as nitrogen is substituted for C—H at the 9 and 9,10 positions in anthracene. At 540°C, the rate constant for the disappearance of PS during carbonization is roughly 100 times greater for phenazine than it is for anthracene. In turn, at this temperature the rate constant for the disappearance of PS during anthracene carbonization is roughly 70 times greater than that for phenanthrene[2]. These results emphasize that major differences exist in the rates of carbonization of polynuclear aromatic compounds, as affected by configuration (shape) of the molecules and the presence of heteroatoms and functional groups.

3.2 Optical microscopy studies

Polished sections of low-temperature carbonaceous residues which were produced by carbonization at different rates to the same level of PI (90%) were examined optically in order to characterize the nature of mesophase formed. A description of the

equipment used is given elsewhere[12]. Table 2 lists the carbonization times and temperatures used for each compound. Unlike the findings of phenanthrene carbonization[2], there were no significant differences in the size of isochromatic regions for low-temperature carbonaceous residues produced at different carbonization rates. Further, there was no significant difference in the size of isochromatic regions for residues produced from different starting compounds. All the carbonaceous residues contained flow domain anisotropy $>50 \mu\text{m}$, that is, isochromatic regions which should be highly graphitizable.

3.3 Calcination

Samples of anthracene, acridine, and phenazine which were carbonized at different rates to the same level of PI (90%) were calcined at 1000, 1200 and 1600°C. Weight loss data are presented in Table 3. As expected, weight loss increases with increasing HTT and with increasing nitrogen content in the organic precursor. Figure 7 presents results for the nitrogen remaining (wt%) in the cokes as a function of calcination temperature. It is estimated that the cokes produced from acridine and phenazine are es-

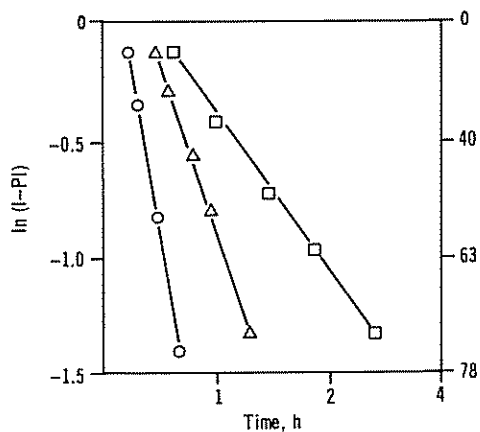


Fig. 5. First-order plots for the formation of PI from acridine: \circ 480, \triangle 460, \square 440°C.

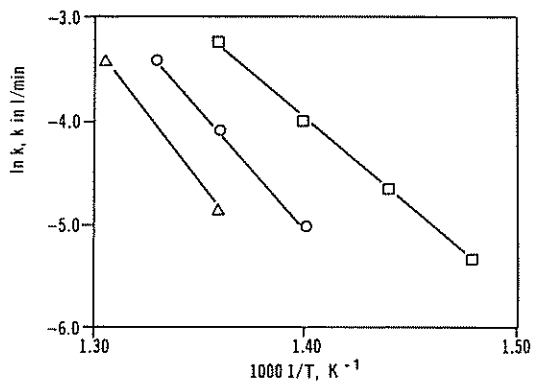


Fig. 6. Arrhenius plots for the formation of PI: \triangle anthracene, \circ acridine, \square phenazine.

Table 1. Parameters for rate constants describing carbonization

Compound	Activation Energy kcal/mole	Pre-exponential, s ⁻¹
Anthracene*	46	4.3 × 10 ⁹
Acridine	42	1.2 × 10 ⁹
Phenazine	35	1.6 × 10 ⁷

*Anthracene values obtained from [1].

essentially free of nitrogen following heating up to 1700°C at 10°C/min and holding for 1 h. In line with previous studies that analyzed the volatiles produced as a result of calcining cokes high in nitrogen[14], it is suspected that N₂ is essentially the only nitrogen-containing species evolved. In line with the findings of Isaacs[14], the additional weight loss found upon carbonization, beyond that due to N₂ release, is attributed primarily to methane release.

3.4 X-ray diffraction studies

Samples of anthracene, acridine, and phenazine which were carbonized at different rates to the same level of PI (90%) were calcined at 1200°C followed by graphitizing at 2500°C. Results are presented in Tables 4 and 5. Consider the cokes first. From the intensity of the (002) X-ray diffraction peak, it is concluded that the crystallite alignment in the anthracene cokes is greater than that present in the cokes derived from acridine and phenazine. However, the cokes derived from the nitrogen-containing compounds exhibit somewhat larger crystallite sizes and smaller interlayer spacings than does the coke derived from anthracene. Superior crystallite alignment continues for the graphitized carbon produced from anthracene coke. Clearly, cokes produced from all three precursors are highly graphitizable with, interestingly, the interlayer spacings in the graphitized carbons produced from acridine and phenazine being smaller than that in the carbon produced from anthracene. Crystallite sizes of all the graphitized carbons are large. Substitution of nitrogen in the ring structure of anthracene at the 9 and 10 positions has little effect on mesophase development during carbonization or, in agreement with Isaacs[14], subsequent graphitizability of the calcined cokes. This has been found despite the fact, as we will see shortly, that cokes and graphitized carbons produced from the nitrogen-containing precursors have lower den-

Table 2. Conditions used to form 90% PI

Compound	Time, min	T, °C
Anthracene	120	525
	180	510
Acridine	90	480
	210	460
Phenazine	90	460
	210	440

Table 3. Weight loss upon calcination of cokes

Calcination Temperatures, °C	Weight Loss, %		
	Anthracene	Acridine	Phenazine
1000	6.7	18.1	19.6
1200	15.2	20.5	23.4
1600	19.4	33.1	33.5

sities than the samples produced from anthracene. Also cokes exhibiting greater crystallite alignment usually exhibit, in turn, greater graphitizability, but this is not found in this case.

3.5 Physical properties of cokes and graphites

Table 6 presents results for the specific surface areas of calcined cokes. At each calcining temperature, anthracene cokes have a lower surface area than the cokes produced from acridine and phenazine. As expected, this is accompanied by the anthracene cokes having higher Hg and He densities than cokes produced from the nitrogen-containing compounds, as seen in Table 7. The Hg density gives the density of the particles, that is particle weight divided by particle external volume. The He density is equal to the particle weight divided by the sum of the volume of crystallites within the particle and pore volume closed to He.

For the anthracene samples, densities increase with increasing HTT, as porosity is removed. Percentage volume shrinkage of the particles exceeds percentage weight loss as temperature increases. On the other hand, particle density goes through a minimum with increasing HTT for the acridine and phenazine. This is a result of percentage weight loss exceeding percentage particle volume shrinkage in the temperature range 1200–1600°C, as large amounts of nitrogen are lost from the cokes.

Knowledge of weight losses (Table 3) and density changes in going from a calcination temperature of 1200°C to 1600°C allows one to calculate changes in particle volume and, thereby, confirm this reasoning. Results are shown in Table 8. The fact that volume losses for the acridine and phenazine cokes were not as large as might have been anticipated in line with the large weight losses, suggests that some compensatory puffing occurred in the temperature range 1200–1600°C as nitrogen was released.

Even though the substitution of nitrogen in the 9 and 10 positions of anthracene had little effect on graphitizability of the cokes produced, its effect on the density of the carbons produced can be quite undesirable. For example, the mechanical properties of carbons rapidly degrade as their densities decrease[15,16].

3.6 Reactivities of cokes in air

Figures 8–10 present reactivity results for the calcined cokes in 0.1 MPa air at 500°C. For the anthracene and acridine cokes, reactivity decreases as

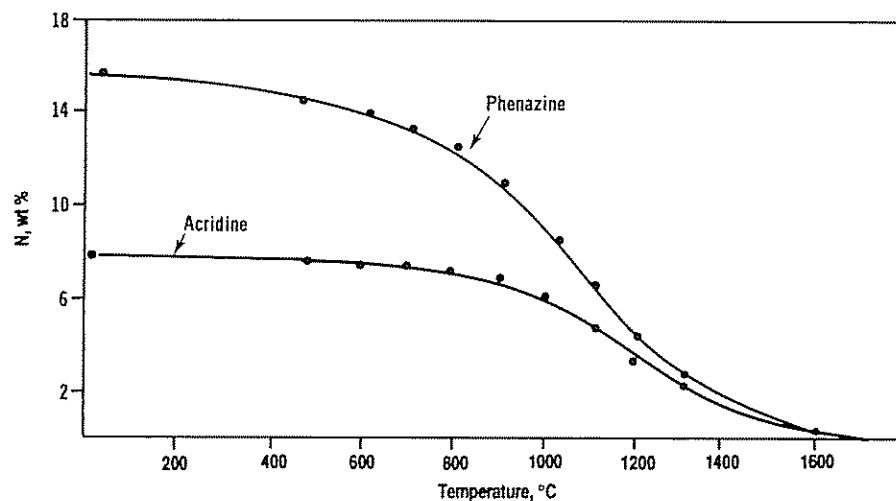


Fig. 7. Nitrogen remaining in cokes as a function of calcination temperature.

calcination temperature increases. Reactivities parallel the decrease in surface area of these cokes with increasing temperature. For the phenazine cokes, reactivity is a maximum for the sample calcined at 1200°C. Again, this parallels surface area data for these cokes which go through a maximum for a calcination temperature of 1200°C. The rate of loss of nitrogen from the phenazine coke is a maximum in the temperature increment 1000–1200°C. It is not accompanied, apparently, by a maximum in particle shrinkage, which then results in a large surface area for the 1200°C sample. It is interesting that upon

heat treatment to 1600°C, the surface area of the phenazine cokes has decreased to a value below that of the acridine coke, as has the reactivity of the phenazine coke. Reactivity of the anthracene coke calcined at 1000°C is lower than reactivities of the acridine and phenazine cokes. This is another indication that nitrogen substitution in the 9 and 9,10 positions of anthracene leads to the production of inferior carbons. Reactivity of cokes to air and CO₂ is of major importance when they are used to produce anodes used in aluminum production. Higher reactivity results in a greater consumption of carbon per unit weight of aluminum produced.

Table 4. X-ray measurements on 1200°C calcined cokes

Coke	$I_R(002)$	d , nm \pm .001	L_a , nm	L_c , nm
Anthracene	11.3	0.347	8.5	1.9
Acridine	10.1	0.345	9.6	2.0
Phenazine	9.7	0.344	11.0	2.7

Table 5. X-ray measurements on 2500°C graphitized carbons

Carbons	$I_R(002)$	d , nm \pm .0001	L_a , nm	L_c , nm
Anthracene	26.1	0.3382	34	73
Acridine	14.4	0.3378	40	69
Phenazine	14.2	0.3380	37	61

Table 6. Surface areas for calcined cokes

HTT, °C	Surface Area, m ² /g		
	Anthracene	Acridine	Phenazine
1000	1.54	5.43	2.38
1200	1.38	3.13	3.69
1600	ND	2.01	1.81

Table 7. Densities of calcined cokes and graphites

HTT, °C	Mercury Density, g/cc	Helium Density, g/cc
Anthracene		
1200	1.983	2.19
1600	1.996	2.22
2500	2.100	ND
Acridine		
1200	1.892	2.06
1600	1.728	1.95
2500	1.870	ND
Phenazine		
1200	1.897	2.04
1600	1.743	1.87
2500	1.880	ND

Table 8. Change in particle weight and volume with increasing calcination temperature between 1200 and 1600°C

Coke	Weight Loss, %	Volume Loss, %
Anthracene	3.8	4.2
Acridine	15.8	7.8
Phenazine	13.2	5.7

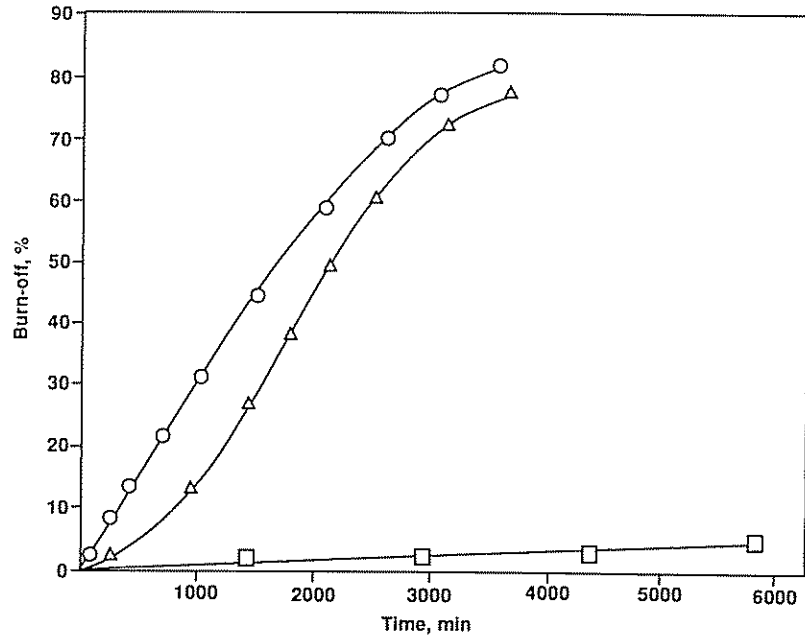


Fig. 8. Burn-off plots for anthracene cokes at 500°C in air: ○ 1000, △ 1200, □ 1600°C.

For the C—O₂ reaction, there is much interest in the CO/CO₂ ratio of the product gas[17]. As has been shown previously, the ratio is a function of reaction temperature, the concentration of active carbon sites, and the fraction of these sites occupied by oxygen surface complex[18,19]. The CO/CO₂ ratio showed a linear decrease with increasing burn-off for the cokes produced from the three precursors. Figure 11 presents results for reaction at 500°C for

cokes calcined at 1200°C. Reaction of air with the anthracene coke yields the highest CO/CO₂ ratio; reaction with the acridine coke produces the lowest ratio. These results suggest two possibilities. The anthracene coke has the lowest amount of active sites covered by oxygen complex during reaction, and/or this coke has a minimum of its active surface comprised of dangling carbon atoms. It is the dangling carbon sites that are expected to lead primarily to

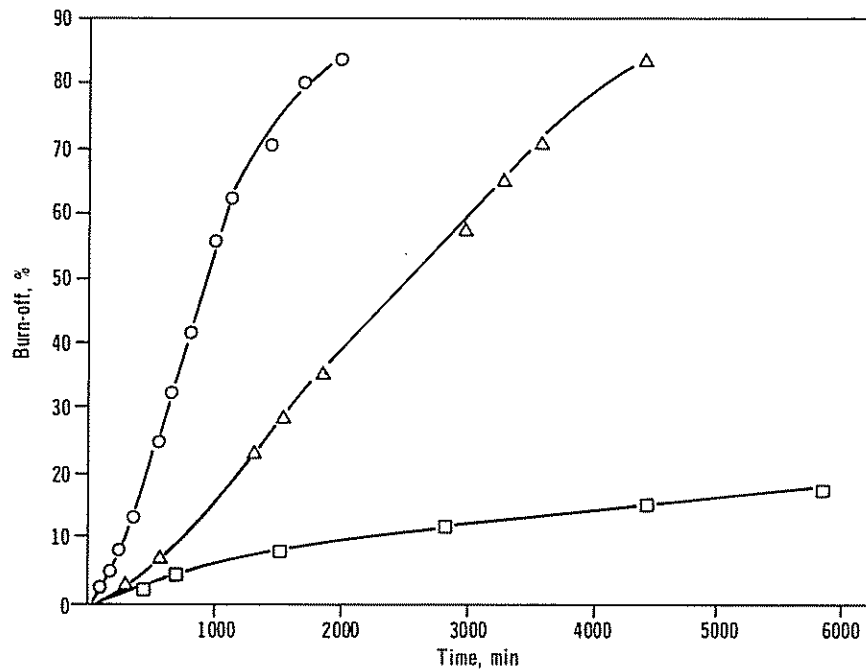


Fig. 9. Burn-off plots for acridine cokes at 500°C in air: ○ 1000, △ 1200, □ 1600°C.

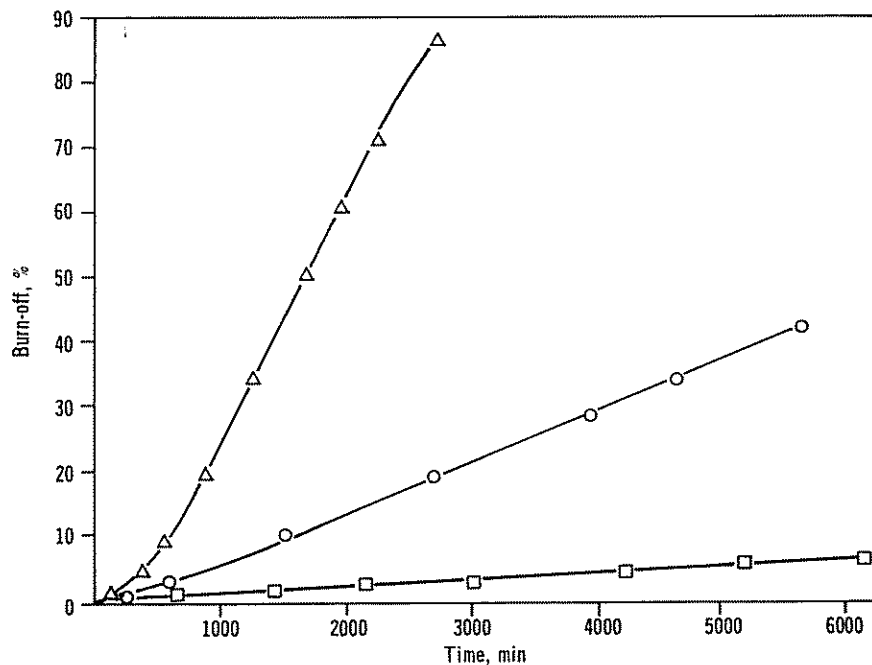


Fig. 10. Burn-off plots for phenazine cokes at 500°C in air: ○ 1000, △ 1200, □ 1600°C.

the production of CO_2 via the decomposition of lactone groups[20]. It would also mean then, as a corollary, that the anthracene coke contains the highest percentage of its surface sites in zig-zag and arm-hair configurations[21], which will lead to the production of CO when oxygen is chemisorbed on them.

4. CONCLUSIONS

Substitution of nitrogen in the 9 and 9,10 positions of anthracene (acridine and phenazine) results in

large increases in rates of carbonization to form PI or low-temperature carbonaceous residues. Whereas crystallite alignment in the calcined cokes and graphites produced from the low temperature cokes are reduced somewhat as a result of nitrogen insertion, graphitizability is little affected. What is affected are particle densities and surface areas. Densities are lower for carbons derived from acridine and phenazine and surface areas are higher, compared to values for carbons derived from anthracene.

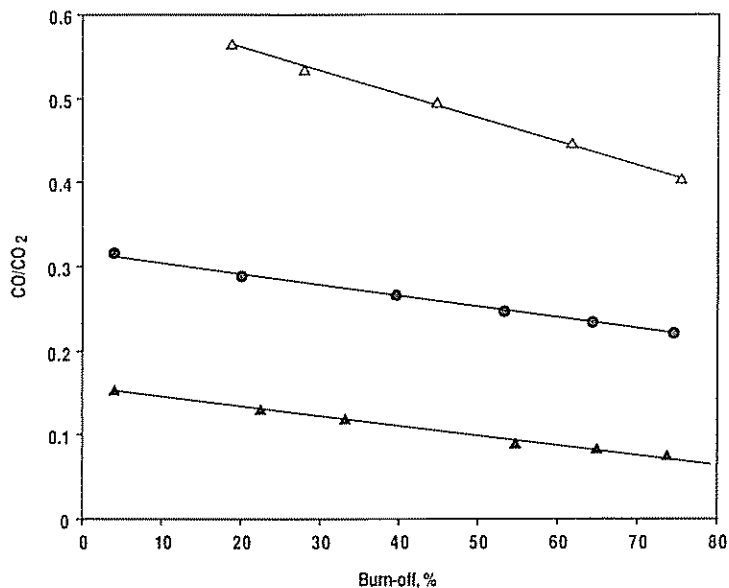


Fig. 11. CO/CO_2 ratios versus burn-off for 1200°C cokes at 500°C in air: △ anthracene, ▲ acridine, ● phenazine.

Acknowledgements—We appreciate having discussions with Dr. R. G. Jenkins. The research was funded by The Pennsylvania State University Cooperative Program in Coal Research.

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