Crystallite Structure of Cokes from Pitch Fractions

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Many carbon products are made by mixing coke with a binder such as pitch, shaping the mass, and baking the product at an elevated temperature. To produce carbon electrodes for the aluminum industry, a mixture containing 10 to 35% of pitch and a coke aggregate is carbonized at 950° to 1100° C. Several tests have been proposed to determine the suitability of pitches for use as binders in the manufacture of carbon products. Martin and Nelson (*12*) suggested that a good pitch should have a high specific gravity and carbon-hydrogen ratio. Charette and Bischofberger (*7*) proposed the use of the product of coking value times carbon-hydrogen ratio.

One of the most important factors is the quality of the "binder coke" which forms from the pitch during baking. Milliken (*11*) and Blayden, Gibson, and Riley (*4*) showed that the type of coke depends upon the chemical constitution of the materials being carbonized and the carbonization procedure. With some exceptions the more aromatic compounds formed the more graphitic cokes. Van Krevelen and Chermin (*13*) observed that the yield of coke on carbonization is greater for aromatic compounds.

Ghosh and Riley (*9*) divided a pitch into three parts by solvent fractionation and showed that on carbonization the insoluble fraction formed a coke with the least graphitic structure. From the results of a modified Kattwinkel test, Brückner and Huber (*6*) concluded that the insoluble fraction acts chiefly as a filler and may even be harmful to coke quality. These results led to the present investigation; for they raised the questions of whether a more extensive fractionation of pitch binders would reveal additional variations in graphitizability, whether any differences existed in graphitizability of corresponding fractions from different pitches, and what the causes of such differences were.

Pitches are tar distillation residues having cube-in-water melting points above 80°F. (*1*). They consist of an insoluble phase, the C-I fraction, dispersed in a continuous phase. The amount determined as C-I depends upon the solvent used in the analytical procedure—good pitch solvents such as carbon disulfide, pyridine, nitrobenzene, or quinoline being generally used. The C-I fraction is derived from three sources: coke or char carried over into the tar during carbonization, carbonaceous matter formed by thermal cracking of tar in the carbonization retort, and insoluble matter formed during distillation of the tar. In low-temperature tars and pitches (Parry process, Lurgi-Spülgas), the C-I is predominantly of the first type. In high-temperature tars (coke-oven, horizontal-retort, oil-gas), the second type predominates. The continuous phase consists of basic, acidic, and neutral materials, each containing a spectrum of organic compounds.

For this investigation five pitches were chosen (Table I) representing three distinctly different types. By means of a series of solvents, each pitch was divided into five fractions; and the structure of the coke from each fraction was determined.

Table I. Properties of Pitches

Pitch	Melting Point, °C.	Quinoline Insoluble, C-I, %	Ash, %
Coke-oven X	110	13.7	0.52
Coke-oven Y	109	16.5	0.26
Coke-oven Z	62	8.9	0.22
Oil-gas	116	13.3	0.96
Lignite, low temp.	109		0.6

PROCEDURE

One hundred grams of powdered pitch were stirred under reflux for 1 hour with five times its weight of solvent. The mixture was filtered through Whatman No. 12 filter paper and the procedure was repeated on the undissolved matter. The undissolved matter was successively extracted by this double extraction procedure with each of a series of solvents. In order of increasing solvency for pitch, the series consisted of *n*-hexane, acetone, benzene, and carbon disulfide. Following Dickinson's nomenclature (*8*) the fractions were called tar oil, resin A, resin B, C-II, and C-I respectively. For two of the pitches, pyridine was used in place of carbon disulfide.

Extraction was easier when raw pitch was treated first with acetone rather than, starting at the beginning of the series, with *n*-hexane. In each case, the amount of solvent was five times the weight of undissolved matter. Solvent was removed from each fraction by distillation at 0.5-atm. pressure. For each fraction yields carbon-hydrogen ratio and molecular weight data were obtained. Molecular weights were determined by the ebulliometric method using nitrobenzene as a solvent. Each fraction was carbonized in argon at a temperature rise of 1° per minute to 1500° C., soaked 4 hours at 1500°, and cooled. Parameters of the crystallites in the cokes were determined by x-ray diffraction using the procedure of Blayden, Gibson, and Riley (*5*).

DISCUSSION

The yield data (Table II) appear normal. The low-melting point coke-oven pitch Z and the low-temperature lignite pitch had the largest tar oil fractions. The lignite pitch contained less C-II and resin B compared with the other pitches. For coke-oven pitches X and Y, carbon-hydrogen ratios of the fractions decreased regularly with increased solubility as was found by Dickinson (*8*). Molecular weights decreased from a value of 1000 for the C-II to 230 for the

Table II. Yield and Properties of Solvent-Fractions of Pitches

	Fraction					
	C-I	C-II	C-II	Resin B	Resin A	Tar oil
	Solvent					
	Insoluble	Pyridine	Carbon disulfide	Benzene	Acetone	*n*-Hexane
Yields						
Coke-oven X	38.1		5.7	15.0	21.4	22.8
Coke-oven Y	28.4	13.1		17.6	21.1	18.2
Coke-oven Z	25.5		7.9	12.9	19.0	37.5
Oil gas	25.2	16.0		15.1	22.0	20.0
Lignite	23.0		2.2	6.0	23.5	43.0
Atomic C/H						
Coke-oven X	2.43		1.87	1.67	1.56	1.45
Coke-oven Y	2.81	1.92		1.62	1.63	1.50
Molecular weight						
Coke-oven Y		1000		800	400	230

Table III. Crystallite Structure of Cokes

Fractions heated at 1°/minute to 1500° C. and soaked 4 hours before cooling.
L_c is crystallite height in Angstroms.
c is interplanar spacing in Angstroms.

	Fraction						
	C-I	C-II	C-II	Resin B	Resin A	Tar oil	Untreated pitch
				Solvent			
Fraction	Insoluble	Pyridine	Carbon disulfide	Benzene	Acetone	n-Hexane	
Coke-oven X, L_c	50.2		72.5	71.0	70.0	70.0	62.5
c	3.47		3.47	3.47	3.47	3.47	3.47
Coke-oven Y, L_c	30.6	71.0		70.0	74.2	[a]	
c	3.51	3.47		3.47	3.46	[a]	
Coke-oven Z, L_c	49.2		71.0	71.5	69.8	71.0	59.8
c	3.48		3.46	3.46	3.46	3.47	3.46
Oil gas, L_c	27.2	59.8		69.0	71.0	65.6	53.0
c	3.52	3.46		3.47	3.46	3.47	3.47
Lignite, L_c	23.4		[a]	43.5	40.2	51.2	47.7
c	3.50		[a]	3.47	3.48	3.47	3.47

[a] Did not form enough coke on carbonization.

tar oil and are somewhat higher than those reported by Dickinson for a coke-oven tar.

X-ray parameters of the cokes from each fraction are given in Table III. Cokes are considered to consist of small graphitelike crystallites suspended in a mass of disordered carbon. In Table III, the parameters refer only to the crystallite phase. Increased heights of the crystallites, L_c, and decreased interplanar spacings, c, indicate more-graphitic cokes. A temperature of 1500° C. was chosen for calcining the cokes in order to accentuate any differences in the crystallite structures. As shown in Figure 1, the spread in crystallite heights between cokes from a graphitizable pitch and from a relatively nongraphitizable pitch is much greater as the temperature increases. The lignite pitch in Figure 1 is not the same as in Table I.

Recently other methods have been used for calculating L_c values from x-ray diffraction curves. Hirsch (*10*) used a Fourier transform method. Alexander and Sommer (*3*) determined the distribution of the numbers of layers constituting the crystallites. With increasing crystallite size, results are obtained (2) by the latter method which approach those obtained by the "width at half-height" method used in this paper and by Blayden, Gibson, and Riley (5). For L_c values of 25 A. the method used by Alexander gives results about 50% lower, and at 50 A. the difference decreases to less than 10%. The width at half-height method was used here because the calculations are simpler, and the relationships among the L_c values upon which the conclusions are based would be unchanged regardless of the method of calculation (2). Moreover, most of the L_c values reported here are in the range where differences due to method of calculation would be of little significance.

For each pitch, coke from C-I had the smallest crystallite height, L_c. In most cases, this was accompanied by a larger interplanar spacing, c. For the other fractions differences were minor, although the lignite and oil gas fractions were less graphitizable than the coke-oven fractions.

Because carbon disulfide is a poorer solvent for coke-oven pitches than pyridine, the C-I obtained with carbon disulfide would be expected to contain some of the other pitch fractions, especially the C-II. That these C-I fractions were contaminated is shown by comparing the crystallite parameters of the C-I from coke-oven pitch Y with those from coke-oven pitches X and Z.

The oil-gas pitch had a less graphitizable C-I fraction than the coke-oven pitches. The C-I from lignite pitch was the least graphitizable of all those tested. This was probably because it consisted of char particles rather than lampblack or other thermal decomposition products.

The tar oil fraction of coke-oven pitch Y did not form enough coke on carbonization for characterization by x-ray diffraction. Tar oil contributes very little to binder coke, as it readily volatilizes during the baking process.

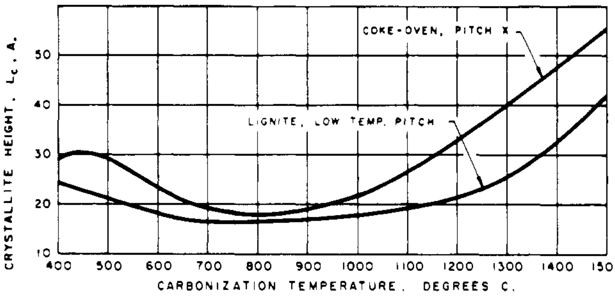

Figure 1. Crystallite heights of pitch cokes as a function of carbonization temperature

For coke-oven pitch X, the uniformity in the crystallite parameters of the cokes from C-II, resin A, resin B, and tar oil indicates that although they differ in molecular weight and carbon-hydrogen ratio, each fraction formed the same type of coke at 1500° C. This might be explained on the assumption that although differing in carbon-hydrogen ratios and molecular weights, the types of hydrocarbons or other compounds present in each of the soluble fractions is the same for a particular pitch. The chemical types initially present influence greatly the graphitizability of the coke formed on carbonization (*4*, *11*).

In all cases, crystallite parameters of cokes derived from binder pitch were intermediate between these of the C-I and the other fractions. If the C-I exerted an effect on the graphitic structure formed by the other fractions, it was not indicated by these data.

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