

Carbons from selected organic feedstocks

PHILIP L. WALKER, JR.

Department of Materials Science and Engineering, The Pennsylvania State University, University Park,
Pennsylvania 16802, USA

Abstract—Carbons in the form of electrodes and anodes, activated carbons, carbon blacks, and cokes and chars (as reducing agents) require large tonnages of petroleum and coal feedstocks for their production. Selected technology for the production of each of these forms of carbon is discussed and possible interchange between petroleum and coal feedstocks considered. The production of carbon fibers used in the fabrication of carbon composites is also considered, since potentially large amounts of feedstocks will be needed for this application. It is concluded that the technology exists to produce carbons with acceptable properties from coal feedstocks in every case, if a shortage of petroleum feedstocks develops. The production of activated carbon from a renewable resource is considered briefly.

INTRODUCTION

THERE CONTINUES to be steady growth in the demand for carbon and graphite products in mature markets, like electrodes, anodes, carbon blacks, and activated carbons. Also there is an excellent potential for large growth in demand for carbons in new markets like carbon composites. Following the recent major increase in the cost of petroleum, which has been the prime feedstock for many of the important commercial carbon products, a renewed interest in the possible increased use of other fossil hydrocarbons (in particular coal) as an organic precursor for carbons has developed. This paper will consider some of these possibilities, along with selected possibilities for specialty petroleum cokes and renewable resources (that is, plant materials).

COKES FOR ELECTRODES AND ANODES

The major use of petroleum as a feedstock for carbon is in the production of graphite electrodes used in the electric arc furnace for steel making (1) and in the production of anode carbons used in the electrolytic reduction of alumina to aluminum (2). Present annual consumption of carbon in the United States in these two applications is approximately 0.12 and 1.5 million tons, respectively. These are both growth markets (throughout the world), and thus there is concern about an adequate supply of suitable feedstock.

Properties of prime importance in electrodes and anodes are: resistance to thermal shock, electrical conductivity, and resistance to air oxidation. These properties are determined to a considerable extent by the degree of alignment of the trigonally bonded carbon crystallites (Fig. 1) which are the building blocks of the carbonaceous filler particles bound together to make the final artifact. This is so since all properties of the trigonally bonded crystallite exhibit a high degree of anisotropy—that is major differences in the basal plane direction compared to perpendicular to the basal plane. Therefore, the very essence of this field is to have a firm understanding of how the nature of the organic precursor and the conditions of carbonization of that precursor affect the degree of crystallite alignment in the coke and graphite produced.

Pioneering studies in this area were made by Brooks and Taylor (3), who were interested in the conversion of coal tar pitches to cokes. They used light microscopy and electron diffraction to follow the carbonization process. They found that when a thermoplastic organic precursor is heated (all organic precursors used for the production of electrodes and anodes are thermoplastic), it melts at some temperature forming an isotropic liquid. Upon heating some thermoplastic precursors to higher temperatures, spheres exhibiting anisotropy in reflected polarized light begin appearing. With increasing temperature and/or time, the size and number of the spheres increase. Ultimately, the spheres coalesce producing a mosaic solid, as depicted in Fig. 2. Typically this process occurs in the temperature range 400–550°C. Whether anisotropic spheres are produced upon the carbonization of a thermoplastic precursor depends upon a delicate balance between chemical and physical phenomena. Planar free radical intermediates

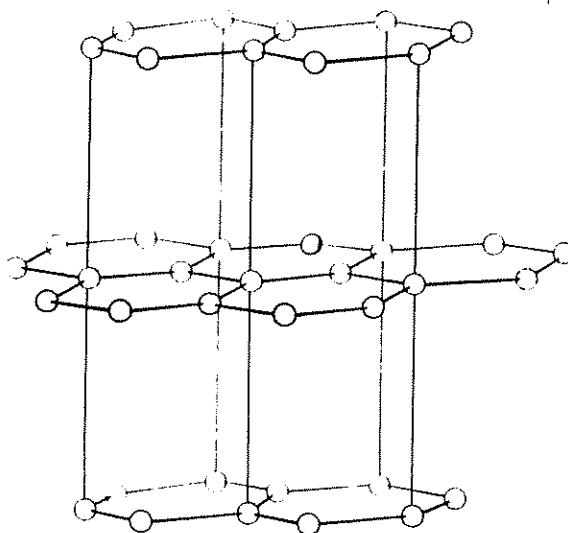


Fig. 1. The arrangement of carbon atoms in the graphite crystal.

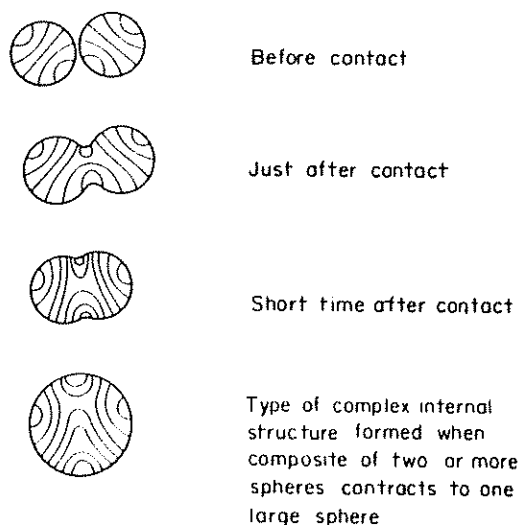


Fig. 2. The morphology of mesophase spheres and their coalescence. Spheres sectioned parallel to main axis of symmetry. Lines depict lamellae (or basal plane) direction (3).

must be produced which upon condensation lead to larger aromatic molecules. Yet the viscosity of the liquid phase must not increase too rapidly, or the aromatic molecules will not have the mobility to align, as a result of van der Waals attractions, and to form anisotropic spheres. These spheres have been called mesophase or nematic liquid crystals.

Weintraub and Walker (4,5) showed the importance of planar free radical intermediates when carbonizing the system phenanthrene ($C_{14}H_{10}$) and biphenyl ($C_{12}H_{10}$). At 0.1 MPa pressure, these compounds melt at 100 and 70°C, respectively. They are mutually soluble at all concentrations. Upon carbonization, phenanthrene (a planar three ring molecule) loses hydrogen, yielding planar free radicals which condense into larger planar sheets. Ultimately mesophase and mosaic structure are produced (Fig. 3). Biphenyl is not a planar molecule, because free rotation is possible around the carbon-carbon bond joining the two aromatic rings together. Upon its carbonization, no anisotropic phase is produced. Weintraub and Walker (4) carbonized mixtures of phenanthrene and biphenyl and then heated the cokes produced to 2800°C to evaluate their

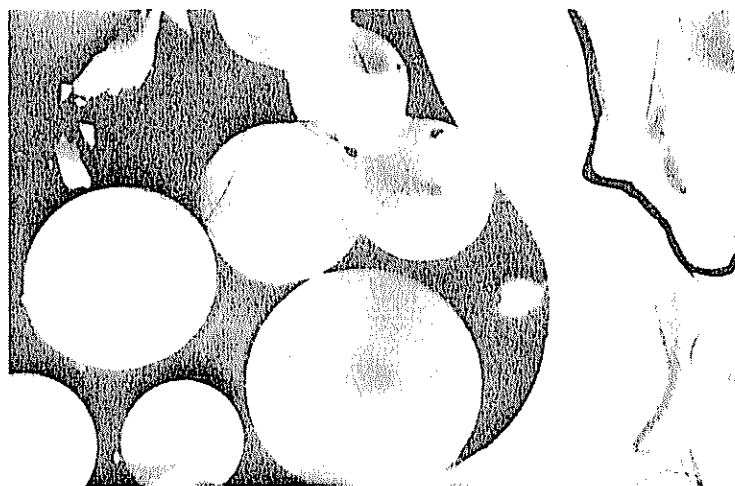


Fig. 3. Mesophase and mosaic structure formed from the carbonization of phenanthrene at 600°C. Micrograph taken in reflected, polarized light. 1000X.

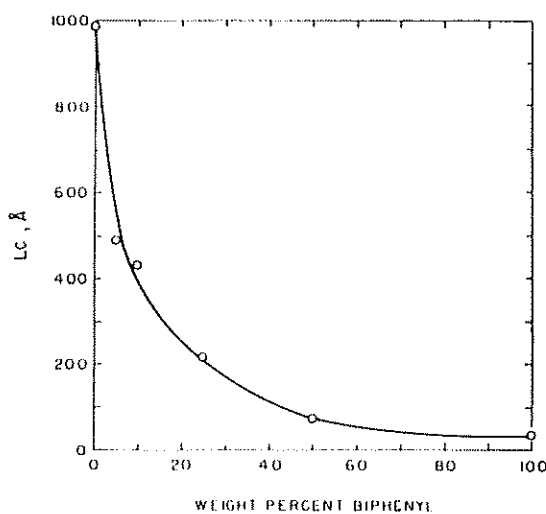


Fig. 4. Average crystallite height in carbons produced following the heating of cokes derived from phenanthrene, biphenyl, and their mixtures to 2800°C (5).

graphitizability using x-ray diffraction. Figure 4 shows the large retarding effect which the addition of biphenyl to phenanthrene has on the extent of crystallite growth (and also crystallite alignment) in carbons produced therefrom. Major differences in physical properties of the carbons produced will also be found.

It follows that the nature of commercial feedstocks will play a dominant role in determining the degree of crystallite alignment in cokes and graphites produced. It is understandable that petroleum cokes of widely varying crystallite alignment are produced, considering that they are derived not only from varying sources of crude oil but also from different refinery streams. Generally, a feedstock low in inorganic constituents, in oxygen and sulfur, and asphaltenes is desired. The presence of oxygen and sulfur can lead to cross-linking reactions between trigonally bonded regions, which restrict mesophase formation. Rigid specifications are placed on the level of inorganic constituents, like titanium, vanadium, and boron, present in petroleum cokes since they will appear to some extent in the final electrode or anode and, hence, the metals being

produced. Further, the inorganic impurities more or less act as catalysts for carbon oxidation. Asphaltenes, in addition to containing relatively high levels of inorganic constituents, also frequently contain organic precursors which generally do not lead to the production of well-developed mesophase.

Differences in petroleum cokes are strikingly obvious, from their photomicrographs, as seen in Fig. 5 (6). The cokes were calcined between 1200–1300°C. Coke #1 is a fluid coke; it is produced in a fluid bed as described elsewhere (7). Cokes #7 and #9 are delayed petroleum cokes; they were produced in a coking drum (8). Shape factors were measured on packed beds of the coke using a liquid permeability apparatus (6). The shape factor (k) equals 6.0 for spherical particles and increases as the particles become more unsymmetrical. Fluid coke particles are closely spherical, they have an "onion shell" type morphology. They have found no use in the production of electrodes and are of limited use in the production of anodes, primarily because of the high coefficient of thermal expansion (CTE) which they impart to the carbon artifact. This high CTE is associated with the poor crystallite alignment which exists within the particles. High CTE frequently causes the artifact to have a poor thermal shock resistance.

Coke #7 is a so-called premium needle coke. It has excellent crystallite alignment (9), resulting in particles which are needle-like in shape upon grinding. Because of good crystallite alignment, shrinkage cracks develop in the solid following cooling from calcination temperature as a result of the major differences in CTE parallel and perpendicular to the basal planes within crystallites (10). Some of these very large cracks are seen in Fig. 6. Upon grinding, crack propagation occurs preferentially along the shrinkage cracks.

Needle cokes are preferred raw materials for the production of extruded electrodes, since they yield artifacts of low CTE (high thermal shock resistance) in the radial direction and high electrical conductivity in the longitudinal direction. These cokes sell for a premium price.

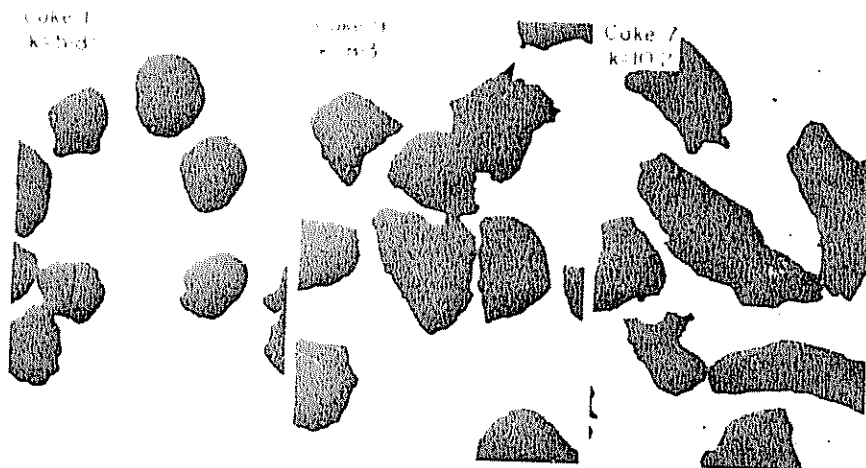


Fig. 5. Photomicrographs of selected petroleum cokes having different particle shapes. 45X (6).



Fig. 6. Texture of a calcined needle-like coke, showing typical flow patterns and large cracks. 40X.

In the manufacture of anodes, used in Hall cells for the production of aluminum, needle coke is not the preferred filler material. That is, anodes are molded; subsequently they conduct current parallel to the molding direction. If the particles are needle shaped they tend to align with their long dimension (or crystallite basal planes) perpendicular to the molding direction. This results in a decrease in electrical conductivity, which is not desirable. For anodes, fillers like coke #9 are more typical. Because the particles are not completely symmetrical, some shrinkage cracks are produced, leading to artifacts having CTE's which are not too high. Generally, the less needle-like the coke is the lower is its price; and, therefore, economics plays a role in the final selection of the filler material.

Following this discussion, it is of interest to consider the potential which other feedstocks have in replacing petroleum in the production of fillers for electrodes and anodes. Coal is the obvious feedstock. In the early days anthracite coal was the prime source of filler carbon for graphite electrodes, but is inferior to most petroleum cokes since it is not as graphitizable and contains too high an inorganic impurity content (11). Its high inorganic content generally rules out its use as a filler for anodes as well (12).

Coal tar pitch, a by-product of the coke oven, qualifies as an important source of coke on the basis of the quality of product which can be produced (9,13). At present it is the prime material used as the binder to hold the filler particles together in electrodes and anodes. Further, a delayed coking plant capable of handling 425 tons per day of coal tar pitch was recently built in Japan to produce filler coke (14). However, there are possibly several limitations to coal tar pitch becoming a prime source of filler coke. First, its supply is limited; and it is not obvious that economics favor the construction of additional coke ovens for the production of coal tar. Second, all coal tars contain more or less quinoline insolubles (13), primarily in the form of carry-over coke dust. The presence of these insolubles is undesirable if a needle coke is to be produced since they reduce the size of anisotropic mesophase formed on carbonization and subsequently its good coalescence to form large mosaic regions (3). Reduction of quinoline insolubles by filtration above the melting point of pitches is possible and, indeed, practiced on a small scale today; but it is a difficult unit operation.

There are at least two other possibilities for the use of coal as a source of filler coke. The National Coal Board, England has been developing a process (15) in which a coal extract is typically obtained from a bituminous coal by solvent extraction, with anthracene oil at around 400°C for about 1 hr. The resulting coal digest is filtered and solvent recovered from the filtrate, prior to its being coked at about 500°C. The coke has been taken to 2500°C to evaluate its graphitizability compared to a coke produced from a petroleum thermal tar. Crystallite growth, both diameter (L_a) and height (L_c), and decrease in interlayer spacing [another measure of graphitizability (16)] were comparable for the two cokes, as seen in Fig. 7.

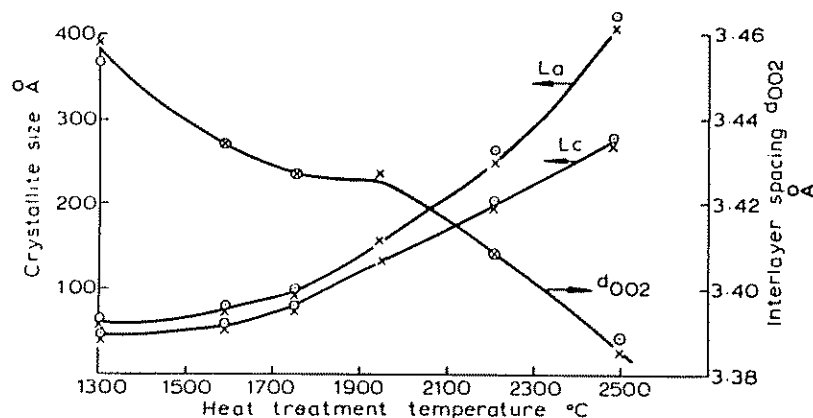


Fig. 7. Changes in crystallite size and interlayer spacing upon heat treatment of a coal extract coke (X) and a petroleum thermal tar (O) to elevated temperatures (15).

Another possibility for the use of coal involves the production of solvent refined coal (SRC). SRC is produced by contacting coals with an organic hydrogen transfer donor and hydrogen gas at typical conditions of 425°C and 20 MPa (17). Following coal liquefaction, the inorganic solids and unconverted coal are separated from the liquid phase by filtration or "antisolvent deashing" (18). The donor solvent is recovered by distillation. Little has been published yet on the use of SRC to produce coke, but some interesting comparisons can be made between this potentially useful precursor and coal tar pitch—both produced from bituminous coal. The most striking difference is that SRC's typically contain a significantly higher concentration of hetero atoms than do coal tar pitches. This is a result of their having been produced at a lower temperature and thus having more functional groups located at the periphery of the aromatic structure and in crosslinks. It has been shown recently in this laboratory that the early stages of carbonization of SRC at 450°C involve the joining together of aromatic molecules originally present, through the elimination of methylene units and condensation of phenolic functional groups (19). The character of the coke produced by further carbonization at higher temperatures, with the elimination primarily of hydrogen, has not yet been studied in this laboratory. It would be thought, however, that crystallite alignment in the coke produced would be a function of the rank of the starting coal. It is expected that, by the year 2000, large amounts of SRC will be produced for use as a boiler fuel and that some of it will be used as a source of coke.

ACTIVATED CARBONS

A broad range of organic precursors are used to produce activated carbon including coal, coconut hulls, acid sludge petroleum coke and wood. Coal is the main organic feedstock. Present annual production of activated carbon in the United States is about 0.1 million tons. Substantial over-capacity is reported, but this situation may change rapidly, as will be seen. The main markets for activated carbon are for water and wastewater treatment, air pollution control, catalyst applications, sugar decolorizing, solvent recovery, purification of chemicals and gases, dry cleaning, rubber reclamation, and auto evaporative control systems. Water and wastewater treatment make up about one-third of the activated carbon market at this time, and it is this application which offers the greatest potential for growth. That is, much notoriety has been given to the recent findings that suspected carcinogenic organics such as carbon tetrachloride and chloroform have been found in drinking water in American cities. The Environmental Protection Agency is considering requiring activated carbon to be used by all water treatment plants following the water chlorination step in order to reduce organic contents down to acceptable levels.

Organic precursors used in the production of activated carbons have in common the important feature that they behave as thermosetting materials. That is, when they are heated to elevated temperatures they show little or no plasticity, probably because they possess a highly crosslinked structure. (This is in contrast to precursors used for the production of cokes, as just discussed.) As a consequence, thermal processing of thermosetting precursors leads to the production of chars, which possess poor alignment of the trigonally bonded carbon crystallites and, hence, contain large porosities and surface areas (both open and closed). The yield of char varies with organic feedstock selected. It depends to a considerable extent upon the amount of hetero atoms (particularly oxygen) in the precursor. These hetero atoms are more or less thermally stable, leaving the precursor as volatile oxides of carbon, hydrogen and hydrocarbons upon carbonization. Yields of chars from American coals, when heated to temperatures of about 950°C, range from a high of about 94%, on a dry mineral matter free basis, for high rank anthracite to a low of 40% for a low rank lignite. The magnitude of the pore volume and surface area and the distribution of pore size produced is a function of the structure of the organic precursor, the maximum heat treatment temperature, and the conditions used for activation (or gasification). All activated carbons contain more or less of their porosity and surface area in macropores, transitional (meso) pores, and micropores. Judicious selection of the organic precursor can lead to the production of activated carbons containing different pore size distributions. All coals have a significant concentration of micropores, that is pores less than 1.2 nm in diameter (20). Low rank American coals (lignites) also have a large concentration of

macropores and transitional pores. By contrast, high rank coals (anthracites) have almost all of their porosity concentrated in micropores (20).

Kawahata and Walker considered the fundamentals of porosity development upon the activation of an anthracite char in 0.1 MPa of CO₂ (21). The principles of their findings can be applied when using other precursors and activating media. Figures 8-10 summarize changes in

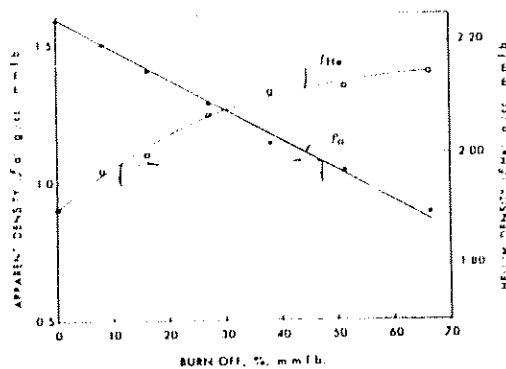


Fig. 8. Variation of apparent and helium densities with burn-off for 42 × 65 mesh anthracite char activated at 850°C (21).

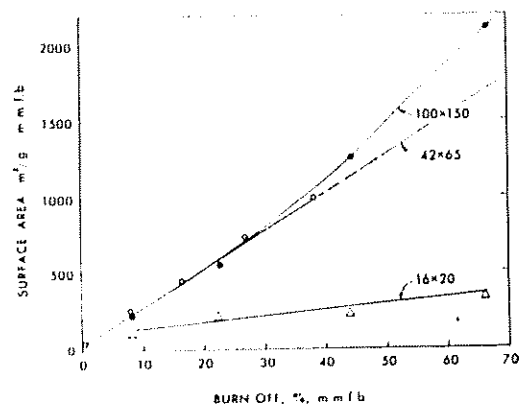


Fig. 9. Variation of specific surface area with burn-off for three particle sizes of anthracite char activated at 900°C. Area measured by N₂ adsorption at 77°K (21).

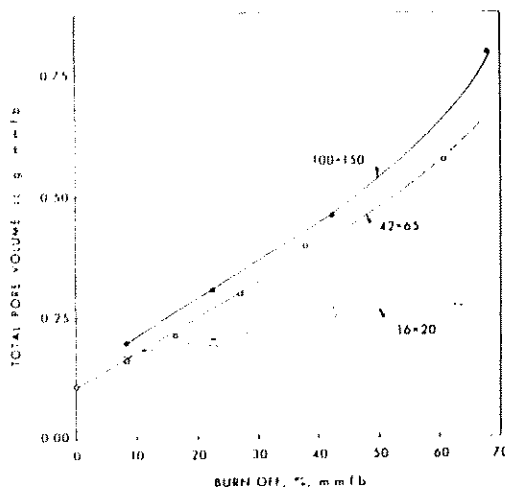


Fig. 10. Variation of specific total pore volume with burn-off for three particle sizes of anthracite char activated at 900°C (21).

densities, specific surface area, and specific pore volume as a function of carbon burn-off. As expected, apparent density of the particles decreases as pore volume within the particle is increased by carbon gasification. All chars, before activation, contain some closed pore volume, that is volume in cavities inaccessible to helium through apertures less than about 0.4 nm in thickness (22). Upon activation, carbon atoms are removed from the apertures, leading to large increases in helium density. As expected, the specific surface area and specific pore volume increase monotonically as carbon burn-off is taken to high levels, since both the number of accessible pores and their average size are increasing. The extent of area and porosity development decreases with increasing particle size being activated because the gasification rate is, in part, mass transport limited. Hashimoto and Silveston (23,24) have attempted to model the activation process using the results of Kawahata and Walker.

Commercially, however, activation is not taken to very high burn-offs since there is a balance between specific area and specific volume and the fact that carbon is being removed by gasification. Figure 11, for example, shows the change in surface area starting with 1 g of char. A similar plot is found for pore volume. Hence, the optimum burn-off for this system would be about 50%. At comparable burn-offs, the surface area developed usually decreases with increasing temperature of activation for the same activating gas. Again this phenomenon is attributed to the gasification rate being, in part, mass transport limited (25).

A potential source of coal-derived chars for activated carbon could be available shortly in line with current interest in the hydrogasification of coal to produce methane. Typically, in hydrogasification, residence time in the reactor at temperatures around 800–900°C is short; coal weight loss is accounted for by volatile matter release and the reaction of hydrogen with the more labile components of the coal. A significant fraction of the fixed carbon content in the coal reacts only slowly with hydrogen and is removed from the reactor as a char. Some of this char will probably be used in gasification with steam to generate hydrogen needed in the process or in combustion to produce power. A breakdown of its uses will obviously depend upon its properties as a function of coal rank and economics.

Samples of char coming from the hydrogasifier reactor of the Hygas Process (26), being developed by the Institute of Gas Technology, have been examined in this laboratory (27). Selected properties of 20 × 65 mesh chars are presented in Table I. Fixed carbon loss denotes amount of carbon burn-off during hydrogasification. At comparable burn-offs, specific surface areas developed fall close to those produced using CO₂ activation for the 16 × 20 mesh anthracite (Fig. 9). It is suspected that greater development of surface area in the hydrogasification chars was limited by diffusional resistance of reactant into the pores of the relatively large particle size used. Nevertheless, pore volumes generated considerably exceed those produced as a result of anthracite activation in CO₂. Ash contents of the chars are high; this is a result, primarily, of the high ash contents in the starting coals. Much of the inorganic phase could be removed by treating

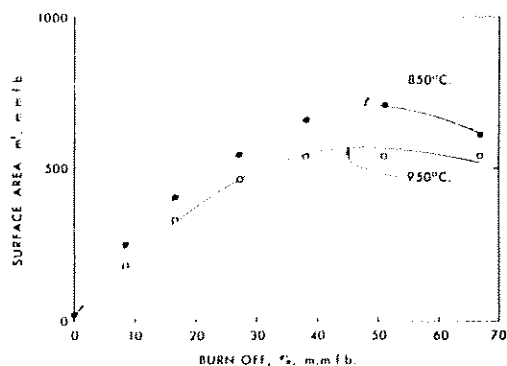


Fig. 11. Variation of surface area with burn-off for 42 × 65 mesh anthracite char activated at 850 and 950°C—basis 1 g of devolatilized anthracite char (21).

Table 1. Selected properties of hydrogasification chars (27)

Coal	Char Properties			
	Fixed Carbon Loss, %	Ash, %	Surface Area, m ² /g*	Open Pore Volume, cc/g
Lignite	33	19.2	531	1.09
Bituminous	39	19.8	396	1.30
Bituminous	23	9.4	300	1.38
Bituminous	42	20.0	396	0.94

*Mineral matter free basis.

the char in warm 10% HCl and then in warm HF, followed by extensive washing and drying (28). Removal of inorganic constituents would introduce additional porosity and surface area into the char.

There is much interest today in understanding how the pore size distribution in activated carbons can be modified by alterations in the over-all activation process. For example, the deliberate addition of metal cations to low rank coals, via ion exchange with hydrogen on carboxyl groups, is reported to affect the structure of chars produced on pyrolysis and the structure of the activated carbon then produced. The use of different gasification media such as oxygen at low temperatures followed by steam or CO₂ at higher temperatures produces some interesting effects (29). Almagro, in this laboratory, has shown that low ash-activated carbons from anthracite can be produced having larger surface areas and pore volumes, if the coal is first exposed to chlorine gas at 950°C prior to conducting activation in steam (30).

There is always an interest in new, abundant organic feedstocks for activated carbon, particularly those which are low in inorganic impurities and will lead to a hard, abrasion resistant product. One such feedstock could be olive stones which are a waste-product from the manufacture of olive oil. Mediterranean countries possess an abundance of these stones, perhaps up to 0.2 million tons per year in Spain, for example (31). Olive stones have a char yield of about 20% (32). Their very low ash and sulfur contents are attractive characteristics. They can be activated to give large surface areas and pore volumes (32).

It is concluded that there is abundant organic feedstock to permit a substantial increase in the world-wide production of activated carbon in the years to come. The use of petroleum as a feedstock will probably be limited since carbons produced therefrom generally have too well ordered a structure to yield high surface area. The only exception known at this time is acid sludge coke, a by-product in the production of white oil. In this process, acid sludges are produced during the sulfonation of oils with strong sulfuric acid. The high sulfur content present in the coke accounts for its disordered structure (probably by acting as a cross-linker). Upon activation of the coke in steam, the sulfur is eliminated and a high purity active carbon is produced. Tars and pitches, which themselves are poor precursors for activated carbons, can be mixed with the sludge to yield a good precursor for activated carbon production (33).

CARBON BLACKS

About 1.5 million tons of carbon black will be produced in the United States in 1978, which represents about 90% of plant capacity. Most of the production will be by the furnace-combustion process, with carbon formation resulting from only partial combustion of liquid petroleum feedstocks in diffusion flames. With the rapid increase in costs of petroleum feedstocks since 1973, there has been some interest shown in the possibility of using feedstocks derived from coal, such as anthracene oil. It is important that the feedstock be highly aromatic and uniform in quality. Feedstocks low in oxygen, nitrogen, and inorganic ash content are also desirable. Most of the tonnage of carbon black produced (about 93% in the United States) is used as a filler to reinforce rubber.



Fig. 12. Electron micrograph of a furnace-combustion black showing crystallite morphology and aggregate of particles. 600,000X (courtesy of L. L. Ban, Columbian Carbon Company).

Carbon blacks consist of essentially spherical particles which are more or less associated into chains or small aggregates (34-36). Carbon blacks range in arithmetic mean diameters from about 500 nm down to 10 nm and, typically, in number of particles per aggregate from 30 to 300 (34). An electron micrograph of a furnace-combustion black, which exhibits considerable agglomeration or structure, is shown in Fig. 12. Within individual carbon black particles, can also be seen small trigonally bonded carbon crystallites. The morphology of carbon blacks is best characterized by the use of gas and liquid adsorption in conjunction with electron microscopy. From electron microscopy measurements of particle size distribution a geometric surface area can be estimated for the black. The adsorption of N_2 at 77°K permits the determination of total surface area of the black, that is geometric area plus area located in open pores within the particles. Adsorption of liquid molecules, too large to enter micropores of the black, are used to measure an area representative of that accessible to rubber (34,35).

Carbon blacks also contain variable amounts of volatile matter depending upon the process used to produce the black (that is channel, furnace-combustion, or furnace-thermal) and how the process is operated. The volatile matter is chemically associated with sites located at the edges of the small trigonally bonded carbon crystallites. It is primarily in the form of carbonyl, carboxyl, lactone, and hydroxyl groups. Depending upon the groups present, the pH of the black will vary from about 4 to 10.

The mechanical properties of black-polymer blends are strongly dependent upon the particle size, structure, and surface chemistry of the black. It has been shown that carbon blacks exhibit free radical properties (37). These free radicals, located at the edges of basal planes, interact with other free radicals generated during polymerization reactions to form covalent bonds. The extent of interaction plays a major role in affecting the mechanical properties of black-polymer blends. Thus, it is clear why the particle size, structure, and surface chemistry of the black are so important. They determine the free radical concentration per unit weight of the black.

In addition to coal possibly assuming an increasing role in the production of carbon black through the use of coal tar pitch or some fraction thereof as a feedstock, there are other possibilities. Johnson and co-workers have shown that when pulverized bituminous coal is dropped in free-fall through a vertical reactor at about 1250°C in the presence of a carrier gas some fraction of the raw coal can be converted to a carbon black as a result of the cracking of the volatiles (38). The black produced resembled a fine thermal black insofar as its surface area and particle size were concerned. Its pH was lower than that generally found for a thermal black, probably because of its higher oxygen content. In compounding with natural rubber, mechanical properties produced, like modulus, tensile strength, elongation, and hardness, were comparable to those obtained when commercial thermal blacks were used.

Another possibility for the use of coal as a feedstock is to gasify it in steam to produce a



Fig. 13. Filamentous carbon produced from the disproportionation of carbon monoxide over iron. 37,000X.

CO/H₂ mixture. Walker and co-workers found that CO could be disproportionated over iron between 500–650°C to give a filamentous carbon and CO₂ (39,40). Key to the process is that H₂ is an accelerator for the reaction. Increasing the amount of H₂ in the CO/H₂ mixture up to at least 40% not only increases the rate of carbon formation but also maintains the iron catalyst in its active metallic state. As a consequence, very large amounts of carbon can be formed per unit weight of iron used.

The crystallinity, surface area, and filamentous character of the carbon formed from CO disproportionation are functions of the CO/H₂ ratio used, reaction temperature, and iron particle size. As seen in Fig. 13, the carbon is primarily in the form of two filaments about 100 nm in thickness, sometimes tightly twisted into a rope and, other times, untwisted. The carbon has an unusually large crystallite size, considering that its formation temperature is around 500–650°C. However poor crystallite ordering results in the carbon being highly porous with surface areas frequently above 100 m²/g. The carbon may be a possible substitute for coarse furnace-combustion or fine furnace-thermal blacks where a high degree of structure is desired.

Attempts have been made for a number of years to produce a substitute thermal black by the fine grinding of coals and cokes to micron size. Particularly active in this area has been Gotshall (41), who has a number of patents on the use of fluid energy mills to carry out comminution (42–46). Following size reduction in a fluid energy mill, to 100% less than 2500 nm, preferably using steam as the grinding medium, the particles are sprayed with a solution containing, for example, zinc stearate in order to coat them with a layer to protect against air oxidation. It is claimed by Gotshall that the finely divided carbons produced are especially preferred for use in vulcanizable rubber compositions because of their ability to materially shorten the relative length of time required to cure such compositions to maximum tensile strength. There is interest in using fluid petroleum coke as the feed material to the fluid energy mill, since it is a relatively low-cost material at this time.

It is difficult to predict whether there will be much change in the selection of feedstocks used to produce carbon blacks in the next two decades. Certainly, the last two decades saw a major shift from natural gas to liquid petroleum feedstocks. This was a result of two factors primarily—perfection of the oil furnace process to produce a black of excellent resistance to abrasive wear and environmental concern about the channel black process which uses natural gas.

COKES AND CHARS AS REDUCING AGENTS

Cokes and chars derived from petroleum and coal feedstocks have an important application in the reduction of metal oxides to metals. Reduction can be accomplished by a solid state

reaction between the oxide and carbon and/or by reaction between the oxide and CO, which in turn is produced by reaction of the carbon with CO.

Coal coke and petroleum coke have been used primarily as reducing agents. Major differences in their reactivity exist, depending upon their crystallite size and the accessibility of the active sites on the crystallites to the reactant gas. For example, delayed petroleum cokes are more reactive than fluid petroleum cokes. This difference is thought to be due to differences in the morphology of the two cokes, as seen in Fig. 5. That is, the active sites in fluid coke, with its "onion shell" structure, are not as accessible for reaction as are the active sites in delayed petroleum cokes.

Major differences in the structure and reactivity of cokes and chars produced from coals are particularly obvious. Figure 14, for example, shows that chars derived from low rank American coals (lignite and sub-bituminous) by thermal processing in nitrogen at 1000°C have much higher surface areas than those produced from higher rank coals (47). There are at least three reasons for this fact. One, chars produced from low rank coals have smaller crystallite sizes. Two, because of larger amounts of volatile matter release from the low rank coals upon heat treatment, the chars produced have a large open pore structure, resulting in greater accessibility of their crystallite surface area. Three, the low rank coals are thermosetting precursors and thus good crystallite alignment does not result upon thermal treatment. This is to be compared with thermoplastic precursors (that is, the medium volatile and some of the high volatile bituminous coals) which lead to coke formation.

As expected from the surface area results, chars produced from lower rank coals have a much higher reactivity to air and CO₂ than do the chars or cokes produced from the higher rank coals (47). As seen in Fig. 15, reactivities of some lignite chars are over one hundred times higher than reactivities of carbons produced from anthracites and low volatile bituminous coals. It has been found recently in this laboratory that reactivities of carbons produced from caking (thermoplastic) coals can be sharply increased if the coal is mildly preoxidized in air at temperatures below 400°C prior to its thermal processing at elevated temperatures. Addition of

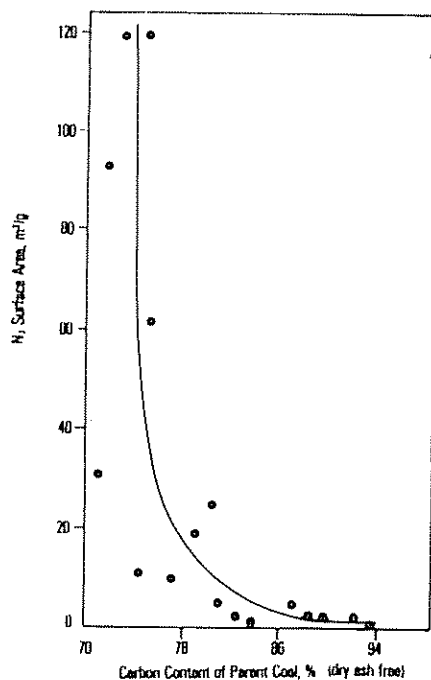


Fig. 14. Correlation between the N₂ surface areas of chars and cokes and the carbon content of the parent coals (47).

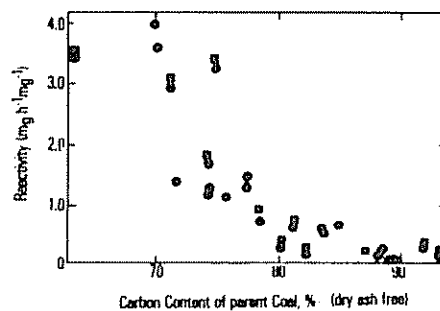


Fig. 15. Variation of reactivity of 1000°C chars and cokes produced from coals of different rank. ● CO₂ at 900°C, ■ Air at 500°C (47).

oxygen to the coals crosslinks trigonally bonded regions and converts the coals from thermoplastic to thermosetting precursors.

It is predicted that chars will be increasingly used as reducing agents, relative to cokes, in the next twenty years. First, supplies of good coking coal are limited. Second, increasing supplies of chars should be available from some coal gasification processes. Third, chars generally have higher reactivities than cokes—certainly for carbon-gas reactions and probably for the direct reduction of metal oxides.

CARBON FIBERS

Carbons discussed so far are part of mature, large tonnage commercial markets. By contrast, carbon fibers used to produce carbon composites are presently associated with low tonnage, specialty markets. However, there is every reason to expect this situation to change by 2000, because of the superior mechanical properties of these fibers. That is, in the basal plane direction, the graphite single crystal has the highest specific tensile strength and Young's modulus of any single crystal. It has been possible in carbon fibers to produce a very high alignment of carbon crystallites, with their basal planes running parallel to the fiber axis, such that much of the high strength in the individual crystallite can be realized in the fiber.

Presently carbon composites are used primarily in sporting equipment and selected aerospace applications. Applications obviously increase as the price of the fibers comes down. There have been major decreases in price from around \$300 a pound in 1970 to a present price of about \$20 a pound. Potentially, the very large market for carbon fibers is the automobile, as the industry attempts to produce a lighter, more fuel-efficient car. Some of the major auto companies are now building experimental "graphite cars", which will decrease the auto weight by about 30%. There are some predictions that the auto and truck market could take 0.5 million tons of carbon fibers each year in the United States if their price can be reduced to around \$5 a pound.

At this time, the main organic precursor for carbon fibers is polyacrylonitrile (PAN) fiber. In turn, the chemical mainly used to produce this fiber is propylene, derived from petroleum feedstocks. A very large amount of research and development work has been done to optimize the process by which PAN fibers can be converted to carbon fibers (48). Such variables as the extent of stretching during spinning of the PAN fiber, extent of oxidation of the fiber at low temperature (about 220°C), extent of stretching during carbonization, and maximum heat treatment temperature affect final properties of the carbon fiber.

More recently, it has been shown to be possible to produce high modulus, high strength carbon fibers from "mesophase pitch" (49). Pitches are heated under quiescent conditions to about 350–450°C to produce liquid spheres which exhibit anisotropic properties, as previously discussed. In order to obtain the desired fibers, a homogeneous bulk mesophase having large coalesced domains up to 0.2 mm in size need to be produced. This requires a pitch low in quinoline insolubles. Most petroleum pitches qualify; most coal tar pitches need to be filtered in

order to lower their solids content sufficiently. Pitches containing from 40–90% mesophase are spun into fibers by conventional techniques, then thermoset in air at around 300°C, prior to their carbonization and graphitization.

Jorro and Ladner have shown that it is also possible to produce high modulus, high strength carbon fibers from coal extracts (50). They used coals having carbon contents ranging from 82.0 to 90.7%. Interestingly, they found that the Young's modulus of strained graphitized fibers was independent of the rank of the starting coal.

In carbon composites the fibers are bonded together by a resin phase, typically an epoxy. Both petroleum and coal feedstocks are used to produce epoxy resins. Thus it is expected that petroleum and coal sources will both be drawn upon to supply the expanding raw material needs for the production of carbon composites in years to come.

CONCLUSIONS

There are increasing uses for carbon in many important, growth markets. Both petroleum and coal feedstocks are now important sources of raw materials used to produce these carbons. If a shortage of petroleum feedstock develops, the technology is at hand to produce increasing amounts of these carbons from coal feedstocks. The production of carbons from renewable resources is limited at the moment, but possibilities exist, particularly for activated carbon.

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