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The physical nature and manufacture of activated carbon

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SYNOPSIS

After defining activated carbon, the author describes its structure and outlines the physical characteristics distinguishing one type of activated carbon from another. The adsorptive properties of these carbons, the raw materials used, and the manufacturing processes—chemical activation, and physical or thermal activation—are outlined. The high-temperature thermal route (which is the most important for the products employed in gold recovery) using coconut shells or coal as the raw material is then discussed in some detail.

SAMEVATTING

Na 'n omskrywing van geaktiveerde koolstof bespreek die skrywer die struktuur daarvan en gee in hooftrekke die fisiese eienskappe wat een soort geaktiveerde koolstof van 'n ander onderskei. Die adsorpsie-eienskappe van hierdie koolstowwe, die grondstowwe wat gebruik word, en die verwaardigingsprosesse—chemiese aktivering en fisiese of termiese aktivering—word in hooftrekke behandel. Die termiese hoëtemperatuurroete (die belangrikste roete wat betref die produkte wat in goudherwinning gebruik word) wat van klapperdoppe of steenkool as die grondstof gebruik maak, word daarna redelik in besonderhede bespreek.

Introduction

Carbonized wood, which can be regarded as a crude form of activated carbon by present-day standards, has been in use for many thousands of years. In about 1500 B.C., the Egyptians, who were aware of the adsorbent properties of wood charcoal, used it for medicinal purposes and as a purifying agent, as did the ancient Hindus, who filtered their drinking water through charcoal[1].

The decolorization and gas-adsorption properties of various carbon products were first investigated in the late nineteenth century, their development having gained impetus from the need for gas adsorbents to protect people against the poisonous gases used in World War I, and also from new applications that arose in the sugar industry and that are related to decolorization.

The ability of activated carbon to adsorb gold from chloride solutions was first reported[2] in 1847. This information attracted considerable interest and, in 1880, Davis[3] patented a process in which wood charcoal was used to recover gold from chloride leach liquors. This process was subsequently to become popular, particularly in Australia.

Shortly after the discovery by MacArthur and the Forrest brothers in 1890 that cyanide was a good solvent for gold[4], Johnson[5] (1894) patented the use of wood charcoal for the recovery of gold from cyanide solutions. Since then, major developments have occurred in the technology relating to the manufacture of activated carbons, which are currently employed commercially in a wide range of industries.

Important applications relate to the use of activated carbons to render water potable by the removal of taste, colour, odour, and undesirable organic impurities, in the treatment of domestic and industrial waste water, in the removal of colour from various types of sugar syrups, in a variety of gas-phase applications, and in the purification of many chemical and pharmaceutical products and foodstuffs. Activated carbon also recently found increased application in the field of hydrometallurgy, particularly in the recovery of gold, silver and, to a lesser extent, molybdenum[6-8].

Despite the commercial importance of activated carbon, little is known outside the industry itself about the raw materials that are suitable for conversion into activated carbon, the methods of manufacture, and the properties that make a product superior for a particular use and apparently unsuitable for another.

In South Africa, the gold-mining industry is the largest single consumer of activated carbon, and it was felt that a paper dealing with general aspects relating to the manufacture of activated carbons, as well as with the properties of the resultant products, would be of interest to personnel in the industry.

What is Activated Carbon?

Activated carbon is a generic term for a family of highly porous carbonaceous materials, none of which can be characterized by a structural formula or by chemical analysis[1]. The volume of the pores in activated carbons is generally defined as being greater than 0,2 ml/g, and the internal surface area is generally larger than 400 m^2/g as measured by the nitrogen BET method. The width of the pores varies from 3 Å to several thousand angstroms, and the pores are generally classified for convenience in terms of their diameters:

Macropores	500	to 20 000	Å
Transitional pores (mesopores)	100	to 500	Å
Micropores	8	to 100	Å.

In cross-section, the pores appear to be cylindrical or rectangular in shape, but can also occur in a variety of

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irregular shapes. Pores may also have constrictions or bottlenecks.

Macropores, which generally contribute very little to the total internal surface area of the product, depend mainly on the nature of the carbonaceous raw material employed and the preliminary manufacturing process, viz grinding and agglomeration of the raw material. Their major function is to serve as transport arteries that make the internal parts of the carbon granules readily accessible to the molecules being adsorbed. The transitional pores account for about 5 per cent, and the micropores for about 95 per cent, of the internal surface area. The micropores are largely the product of the activation process.

Activated carbons are commercially available in numerous forms: powders, granular chips in various size ranges, and shaped or moulded products extruded into rod-like shapes, which are commonly 0,8 to 6 mm in diameter by 3 to 10 mm in length.

Structure

X-ray-diffraction studies have shown that the structure of thermally activated carbon is similar to that of graphite[9,10]. Ideal graphite, as shown in Fig. 1, consists of layers of fused hexagons held approximately 3,35 Å apart by Van der Waals forces, so that the carbon atoms in any one plane lie above the centres of the hexagons in the layer immediately below it. The lattice is of the ABAB type.

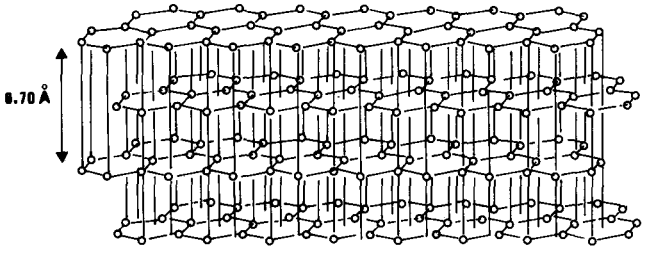

Fig. 1—Schematic representation of the structure of graphite; the circles denote the positions of carbon atoms, while the horizontal lines represent carbon-to-carbon bonds (after Bockris[9])

The proposed structure of thermally activated carbon is depicted in Fig. 2. The carbon is believed to be composed of tiny graphite-like platelets, only a few carbon atoms thick and 20 to 100 Å in diameter, which form the walls of open cavities of molecular dimensions, i.e. the pore system. However, the hexagonal carbon rings, many of which have undergone cleavage, are randomly orientated, and lack the directional relationship with one another that is present in single graphite crystals. The overall structure is therefore very disordered, and is often referred to as 'turbostratic'. Furthermore, the separation between the layers is greater than that found in graphite, viz 3,60 Å.

Because of the high level of structural imperfections in activated carbons, there are many possibilities for reactions with carbon atoms at the edges of the planar layers. As a result, oxygen-containing organic functional groups, which are located mostly at the edges of broken graphitic ring systems, are present on the surface of the carbon.

Although the exact chemical structures of these surface oxides are not known with certainty, it has been suggested that the surface oxides depicted in Fig. 3 are the oxides most often present in thermally activated carbons[10]. Basic surface groups have also been identified, and it appears that the nature of the surface groups depends upon conditions during and after manufacture[6].

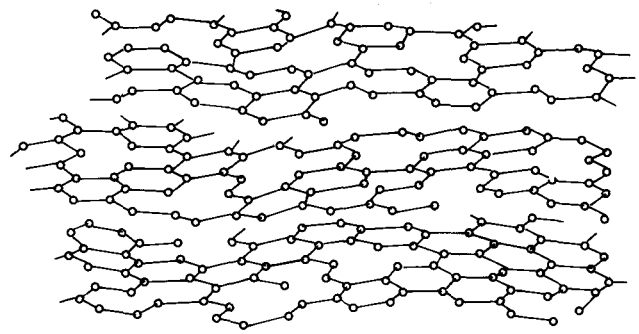

Fig. 2—Schematic representation of the proposed structure of activated carbon; oxygen-containing functional groups are located at the edges of broken graphitic ring systems (after Bockris[9])

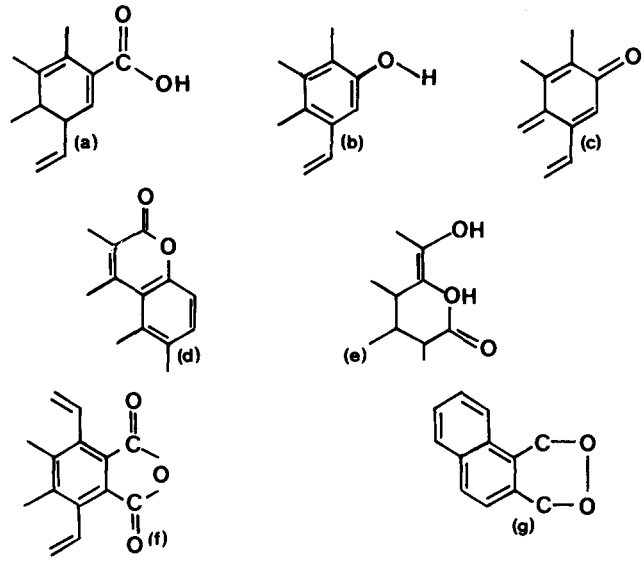

Fig. 3—Structure of some surface oxides[10]: (a) carboxylic acid (b) phenolic hydroxyl (c) quinone-type carbonyl groups (d) normal lactone (e) fluorescein-type lactones (f) carboxylic acid anhydrides (g) cyclic peroxides

Characterization of Activated Carbons

The different types of activated carbon can be distinguished from one another only by reference to certain physical and chemical properties.

Important physical properties are the number and size distribution of the pores, bulk density, dry impact hardness, wet abrasion resistance, and particle-size distribution. From the chemical point of view, comparisons are based on the ability of the different products to adsorb various selected substances from the gaseous phase, e.g. benzene, carbon tetrachloride, and nitrogen, as well as from the aqueous phase, e.g. iodine, molasses, phenol, methylene blue, and tannin.

For example, the nitrogen BET value expresses the surface area in square metres per gram of adsorbent that

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can be covered by nitrogen in a monomolecular layer. Activated carbons typically yield values between 400 and 1500 m^2/g, the former value corresponding to what is termed a low-activity product and the latter to a high-activity product. Such surface-area dimensions alone are insufficient to characterize a carbon product, simply because the nitrogen molecule is very small and can therefore penetrate into pores that are not accessible to other larger molecules. Hence, for the practical assessment of activated carbons, the adsorptive capability of the various products for compounds of large molecular dimensions, viz molasses, methylene blue, and tannin, is determined under standard experimental conditions.

The extent to which the various activated carbons adsorb molecules of a different size can be regarded as an indication of the distribution of their internal accessible volume among pores of different sizes. Hence, the small iodine molecule is adsorbed in pores down to 10 Å in diameter so that the iodine number is an indication of the surface area of the pores in that size range. At the other end of the scale, molasses, a large polysaccharide molecule, is adsorbed only in pores larger than about 30 Å in diameter, and the molasses number gives an indication of the number of pores in that size range[8].

A more sophisticated method by which information about the pore-size distribution can be gained involves measurement of the pressure required to force liquid mercury into the activated carbon. This, in turn, can be related to the size of the pore into which the mercury is being forced. The pore-size distributions shown in Figs 9 and 11 were obtained by this method.

Those physical and chemical properties most often employed by manufacturers of activated carbon to characterize their products are listed in Table I. Typical values are indicated for a high-activity coconut-shell carbon, which is activated thermally using steam, and which is usually employed in gas-phase applications and in processes for the recovery of gold from cyanide leach liquors.

TABLE I
PHYSICAL PROPERTIES AND CHEMICAL-ADSORPTION CHARACTERISTICS OF A THERMALLY ACTIVATED COCONUT-SHELL CARBON TYPICAL OF THOSE EMPLOYED IN GOLD-RECOVERY APPLICATIONS

Physical properties	
Particle density (mercury displacement)	0,80 to 0,85 g/ml
Bulk density	0,48 to 0,54 g/ml
Pore volume	0,70 to 0,80 ml/g
Ball-pan hardness (ASTM)	97 to 99%
Particle-size distribution	1,18 to 2,36 mm
Ash content	2 to 4%
Moisture content	1 to 4%
Chemical-adsorption characteristics	
Surface area (nitrogen BET)	1050 to 1200 m^2/g
Iodine number*	1000 to 1150 mg/g
Carbon tetrachloride number†	60 to 70%
Benzene number	36 to 40%

* The iodine number indicates the mass of iodine adsorbed out of aqueous solution under standard experimental conditions by 1 g of activated carbon

† The carbon tetrachloride number indicates the mass of carbon tetrachloride vapour adsorbed under standard experimental conditions by 1 g of activated carbon, expressed as a percentage

Adsorptive Properties

It is generally conceded that activated carbon owes its adsorptive properties primarily to its large internal surface area, as well as to its pore-size distribution, and that the external surface area and the nature of the surface oxides play minor roles[6,10]. The size of the pores developed during activation therefore has an important influence on adsorption behaviour because the pores act as a screen. This screen prevents the adsorption of large molecules, but promotes the adsorption of an adsorbate that fits snugly into the pores, making the maximum number of contacts with the adsorbed molecule, and thus maximizing ΔH as defined in equation (1):

$$\Delta H = \Delta G + T\Delta S, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where

ΔH is the change in free enthalpy,
ΔG is the change in free energy,
ΔS is the change in entropy, and
T is the temperature of the system.

Fig. 4 attempts to illustrate this concept for the case in which two adsorbate molecules in a solvent, which is not shown, compete with each other for adsorbent surface or sites. The external surface can provide only a certain amount of access to the inner pores, and it is likely that the main role of the surface oxides is to impart a hydrophilic character to the predominantly hydrophobic carbon skeleton. This would account for the affinity of activated carbon for many polar and non-polar organic and inorganic species[8].

Activated carbon functions by adsorption, i.e. by the adhesion of certain substances to the internal surface constituting the walls of the pores. Hence, the greater the adsorption surface available, the better is the adsorption function.

Adsorption occurs as the result of an imbalance of the forces that act upon the carbon atoms constituting the surface of the pore wall. Such an imbalance is inherent in all surfaces and, in an attempt to rectify it, molecules are adsorbed from the gaseous or aqueous phases, and are attracted and held to the surface. Surface adsorption, regardless of the energy of the interaction, must always proceed with a negative change in free energy (ΔG), as well as a decrease in entropy (ΔS), which, according to equation (1), must result in a negative change in free enthalpy (ΔH). Hence, adsorption is always an exothermic process[10].

There are two types of adsorption process: physical and chemical adsorption. Physical adsorption involves weak Van der Waals forces (also dipole–dipole interactions and hydrogen bonding), and the processes are generally reversible. Chemical adsorption refers to processes involving homopolar forces (as in ionic or covalent bonds), and such processes are generally irreversible. Nevertheless, in most instances, the adsorptions can be classified as being physical in nature.

In general, the factors that influence the adsorptive behaviour of activated carbon from aqueous solution are temperature (adsorption generally decreases with increasing temperature); the pH value of the solution (carbon generally has a low affinity for ions, particularly those with a high charge-to-surface ratio, and pH can affect

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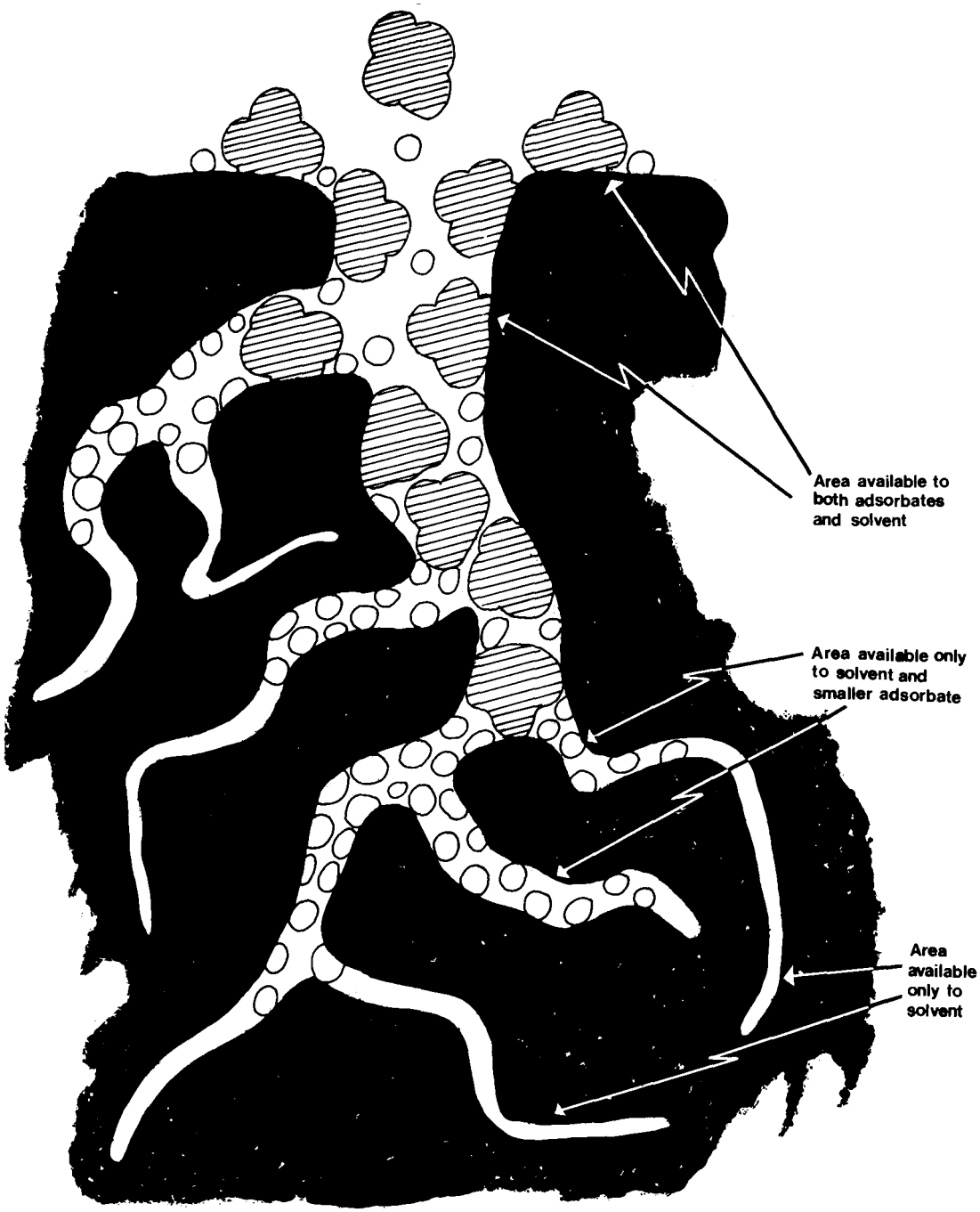

Fig. 4—Concept of molecular screening in micropores (after Pittsburgh Activated Carbon Brochure[11])

ionicity); the chemical nature of the species present and their relative concentration; and the nature of the activated carbon and its particle-size distribution. For molecules to be adsorbed, they must reach the internal surface of the macropores by diffusion. Therefore, the reaction time will be influenced by the length of the diffusion path, and the kinetics of adsorption will increase with decreasing particle size.

Activated carbon is a very versatile substrate with respect to its interactions with various organic and inorganic compounds. It is able to function as a simple adsorbent that is akin to synthetic polymeric adsorbents, since molecular compounds can be physically adsorbed onto its large internal surface area, and be retained there by forces of the Van der Waals type[7,8]. It can also function as a reducing agent or, in the presence of excess oxygen, as an oxidation catalyst[1,7,10]. As a result, the adsorption of organic and inorganic species onto carbon may occur by several mechanisms, and their identification, particularly in the extraction of certain metal complexes from solution, is extremely difficult as in the extraction of the gold dicyanoaurate anion[12-14].

Because carbon is generally a non-polar material, it adsorbs organic compounds in preference to polar inorganic species. For example, small highly charged cations such as Ni^{2+} and anions such as Cl^- are not adsorbed by activated carbon to any significant extent[13].

The adsorption of organic species onto carbon usually

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occurs by simple mechanisms that are fairly well understood in terms of a balance between hydrogen-bonding forces in solution and Van der Waals attraction between the carbon surface and the organic compounds. The driving force for the adsorption of organic molecules onto carbon is similar to that responsible for the salting-out of organic materials dissolved in water, where the addition of a simple inorganic salt causes the organic material to separate out from the aqueous phase[8].

These considerations have given rise to the statement frequently made that adsorption onto activated carbon is a fight against solubility. Applications involving organic materials will therefore be most attractive when the adsorbate has high molecular mass, low polarity, and a low degree of ionization, because these properties generally signify low aqueous solubility. Hence, activated carbons are excellent adsorbents for a considerable number of aliphatic compounds, and particularly for aromatic compounds like those commonly found in pesticides and herbicides. As such, activated carbons are employed extensively, not only in commercial applications that require the removal of contaminating organic compounds from aqueous effluents, but also in purification and recovery processes[6,10].

Because granular activated carbons are expensive, their application is usually economically viable only if the carbon can be regenerated and therefore recycled in the process.

The regeneration of granular activated carbon is generally accomplished using steam, hot solvents, or thermal routes. Regeneration by extraction with steam can be applied if the carbon contains substances that volatilize at temperatures below 150°C. For substances of higher boiling points that pyrolyse on heating, thermal reactivation at 700 to 950°C is employed. Steam is usually injected into the kiln, and any pyrolysed organic substances, i.e. non-volatile carbonaceous materials, that may be present in the carbon are burnt away by the reaction shown in equation (2):

$$C + H_2O \rightleftarrows CO + H_2 \ (\Delta H = 29 \text{ kcal/mol}). \ .. \ (2)$$

This treatment cleans the pyrolysed contaminant carbon from the walls of the pores, and returns the carbon to its original activity. It should be noted that the pyrolysed residue is indistinguishable from the original carbon, and care should therefore be taken to ensure that not too much of the original carbon matrix is burnt away during thermal reactivation.

Regeneration can also be accomplished by treatment of the spent carbon with a solvent in which the adsorbate is highly soluble. The preferred route will depend on whether recovery of the adsorbate is desired or not. If it is, regeneration using steam or solvent extraction is preferred.

Manufacture of Activated Carbons

The most important step in the production of activated carbon is activation. This is the process by which the chosen raw material or carbonized raw material is converted into a finely crystalline form of carbon that is permeated by the greatest possible number of randomly distributed pores of various shapes and sizes. These pores give rise to the extended internal surface area. In the manufacture of activated carbon, it is desirable to develop the maximum accessible surface area that is commensurate with economic viability and product application[10,15-17].

The products of simple coking or carbonizing (such as that used in the early days) do not meet present-day standards. This can be attributed to the fact that the available surface area of pulverized charcoal, which is essentially external surface area, is only 2 to 4 m^2/g—as against typically 1000 m^2/g for a granular activated-carbon product—measured by the nitrogen BET method.

Raw Materials

Activated carbon can be manufactured from any carbonaceous raw material, and numerous patents have been granted for processes using such diverse starting materials as various ranks of coal (peat, lignite, bituminous coal, and anthracite), coconut shells, peach and apricot stones, waste tyres, wood, sawdust, petroleum heavy oil, cellulose, rice husks, corn cobs, sugar, bones, etc.[10,16,17]. All the starting materials used in relatively large-scale manufacture are readily available and, hence, are reasonably priced[15]. In the Western World, the companies entering the business in the past 30 years have tended to concentrate on using coal (mostly lignite, bituminous coal, and anthracite), whereas, in the developing world, new entrants have concentrated on using coconut-shell charcoal.

Since the manufacturing process involves the removal of volatile matter from the raw material, the economic relationship between the price, availability, and quality of the raw material on the one hand, and its volatile content on the other, is important. For example, one of the advantages of bituminous coal and anthracite is their relatively low volatile content (as shown in Table II) and, hence, their high yield of product[15].

TABLE II
FIXED CARBON CONTENT OF RAW MATERIALS COMMONLY EMPLOYED IN THE MANUFACTURE OF ACTIVATED CARBON (AFTER HOLDEN[12])

Material	Approximate carbon content, %
Soft wood	40
Hard wood	40
Coconut shell	40
Lignite	60
Bituminous coal	75
Anthracite	90

In the developing world, a major consideration is the availability of waste materials such as coconut shells and rice husks, which, despite having very high volatile contents and, hence, giving low yields of activated carbon, are so inexpensive that the economics involved in their use are often favourable.

Although the activation procedure and the after-treatment employed mainly determine the chemical nature of the surface oxides and the surface area of the resultant product, the structure of the pores and the pore-size distribution are largely predetermined by the nature of the starting material.

This paper focuses on the various steps involved in the

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manufacture of activated carbon from coconut-shell charcoal and from coal, as well as on the properties of the resultant products.

Chemical Versus Physical Manufacturing Processes

Although the general outlines of the various manufacturing processes are well known, the exact details of the procedures employed by the manufacturers are jealously guarded secrets. In general, the methods most commonly employed for the manufacture of activated carbon are of two main types: the wet-chemical process (basically a single-stage process), and the physical or thermal–gas process (essentially a two-stage process).

As would be expected, chemical methods use chemicals for activation, whereas thermal processes use gases (usually carbon dioxide and air), vapours (steam), or mixtures of gases and vapours[15-17].

Chemical Activation

The wet-chemical process is generally employed to convert uncarbonized cellulosic material, primarily wood, into activated carbon. The most popular activating agent is phosphoric acid, although zinc chloride and sulphuric acid are also well-known agents. Other chemicals also suggested for use include sodium carbonate, sodium and calcium hydroxide, and the chloride salts of magnesium, calcium, ferric iron, and aluminium. These chemicals have in common only their strength as dehydrating agents.

The process using sawdust as the starting material involves mixing of the raw material and the dehydrating agent into a paste. The paste is then dried and carbonized in some type of kiln, usually a rotary kiln, at between 200 and 650°C. Upon calcination, the impregnated chemicals dehydrate the raw material, resulting in charring and aromatization of the carbon skeleton, with the concomitant creation of a porous structure and extended surface area.

This procedure yields a power product. If a granular product is required, granular materials are simply impregnated with the activating agent, and the same general procedure as that described above is followed. However, these granular products are generally soft (unless they are manufactured from the powder after suitable pelletization), which limits their application.

After carbonization of the paste, the activating agents are usually recovered and recycled for economic reasons. All the commonly used chemical activators impose certain constraints on the overall activation process and the equipment employed, or on the quality of the product. Mixtures of sulphuric acid and wood cannot be heated above 200°C, and the product, after the sulphuric acid has been recovered by leaching, has adsorptive properties only when wet. Activation with phosphoric acid requires temperatures in the range 375 to 500°C, and the reagent is readily recovered by leaching with water. However, corrosion of the equipment is a major problem. Activation with zinc chloride occurs in the temperature range 550 to 650°C and, although most of the zinc chloride is recovered by leaching with dilute hydrochloric acid, problems may arise in the application of the product because it retains traces of zinc salts. The activated carbon produced with phosphoric acid and zinc chloride can be dried with little, if any, loss of adsorptive capacity.

The activity of the product can be controlled by alteration of the proportion of raw material to chemical reagent. For phosphoric acid, the proportion is usually between 1:0,5 and 1:4. The activity, as measured by the number of pores created, increases as the proportion of the chemical activator increases, and is also affected by the temperature and residence time in the kiln.

Physical or Thermal Activation

The first step in the production of activated carbon by the thermal route is carbonization, which is the formation of a char from the source material. Carbonization is generally accomplished by heating of the source material—as lumps or pre-sized material, or in moulded form, e.g. as briquettes or extrudates—in an inert atmosphere such as flue gas to a temperature that must not exceed 700°C so that dehydration and devolatilization of many of the carbon atoms can occur in a controlled manner. The main purpose of carbonization is to reduce the volatile content of the source material (a fixed carbon content of 80 per cent or higher is desirable) to convert it to a suitable form for activation. Rearrangement of the carbon atoms into graphitic-like structures also occurs during carbonization.

As previously mentioned, the process by which the carbonized product develops an extended surface area and a porous structure of molecular dimensions is referred to as *activation*. This step is generally conducted at temperatures between 800 and 1100°C in the presence of a suitable oxidizing agent such as steam, air, carbon dioxide, or any mixture of these gases. The active oxygen in the activating agent burns away the more reactive components of the carbon skeleton as carbon monoxide and carbon dioxide, depending on the oxidizing agent employed. Although the burning-out of the carbon skeleton to create new pores is believed to occur at different rates on different parts of the exposed surface, the detailed mechanism of this process is not clearly understood.

According to Smisek and Cerny[16], gasification of the carbonaceous material by steam and carbon dioxide occurs in accordance with the endothermic reactions shown in equations (2) and (3):

$$C + H_2O \rightleftharpoons CO + H_2 \ (\Delta H = 29 \text{ kcal/mol}). \quad .. \quad (2)$$

$$C + CO_2 \rightleftharpoons 2CO \ (\Delta H = 39 \text{ kcal/mol}). \quad ..... \quad (3)$$

The reaction of water vapour with carbon is accompanied by the secondary reaction of water–gas formation, which is catalysed by the carbon surface as shown in equation (4):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \ (\Delta H = -10 \text{ kcal/mol}). \quad (4)$$

Because the reactions of carbon with steam and carbon dioxide are endothermic, the activation process lends itself to accurate control of the conditions in the kiln. External heating is required to drive reactions (2) and (3), and to maintain the reaction temperatures. However, as shown in equation (5), the reaction of carbon with air (oxygen) is extremely exothermic:

$$C + O_2 \rightleftharpoons CO_2 \ (\Delta H = -97 \text{ kcal/mol}). \quad ..... \quad (5)$$

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This reaction is difficult to control, and excessive burn-off of the external carbon surface can easily occur, resulting in a decrease in average particle size, which obviously reduces the yield of final product. The reaction of steam with carbon is catalysed by certain chemicals (e.g. the oxides and carbonates of alkali metals, iron, copper, and other metals), and some commercial operations use these chemicals as catalysts. Therefore, as combustion proceeds, preferential etching occurs, which results in the development of a large internal surface area and the creation of a pore structure.

The art of the manufacturer of activated carbon lies in conducting the activation process in such a way that combustion of the carbonized raw material occurs internally, and not from the exterior of the granules. The term *burn-off* is used to denote the degree of activation, which is the loss of char (in percentage by mass) that is allowed to occur. The burn-off (B) and activation yield (Y) are related as indicated in equation (6):

$$B = 100 - Y. \quad \ldots\ldots (6)$$

Carbonization and activation used to be carried out separately, but there is currently an increasing tendency for the two processes to be conducted in the same kiln. A wide variety of furnaces and kilns are used for carbonization and activation, including rotary kilns fired directly or indirectly, multiple-hearth furnaces, fluidized-bed reactors, and vertical retorts, each of which has advantages for a particular purpose. The indirectly fired rotary kiln, for example, is relatively large and expensive, but avoids a large discharge of inert gases to the afterburner. The fluidized-bed reactor is extremely compact, but is generally used only for the activation of abrasion-resistant raw materials because of the attrition that occurs during fluidization.

The effect of the heat treatment of a carbonaceous material on its resultant structure is as follows[16]. As the temperature of carbonization increases, polymerization occurs and, irrespective of whether the starting material is composed of long-chain aliphatic or aromatic molecules, a system of planar condensed benzene-ring molecules is formed. A solid then forms (this is possible at a range of setting temperatures) as a result of the formation of C – C bonds between neighbouring planes. From 400 to 700°C, these condensed ring systems grow gradually, but all the peripheral carbon atoms are attached by chemical bonds to hydrogen atoms or to hydrocarbon groups. Hence, these substances are termed condensed molecular solids, and have high electrical resistivity, which is typical of chemically activated carbons. However, between 700 and 800°C, many of the hydrogen atoms or hydrocarbon groups are expelled from the material, leaving small crystallites having a structure similar to that of graphite. The evolution of gases coincides with a drastic reduction in electrical resistivity.

Moulded forms of the raw material, e.g. briquettes or extrudates, are obtained as follows. The wood charcoal, coal, or peat used in the raw material is pulverized, and the powder is mixed with a coking binder. The hot mixture is then pressed into briquettes, or is extruded through dies into rod-like shapes of a selected diameter. Powder carbons are obtained by the crushing and grinding of granular material.

If cognizance is taken of the many combinations of source material and conditions for carbonization and activation that can be employed in the manufacturing process, it is apparent that a large number of activated-carbon products can be obtained. Because, as previously discussed, no clearly defined chemical formulae can be determined for these products, the only way in which they can be distinguished from one another is by reference to selected physical and chemical properties.

Properties of Activated Carbons

The most significant differences between chemically and thermally activated carbons relate to pore-size distribution (Fig. 9) and semiconductor properties.

Chemically activated carbons are generally characterized by a macroporous pore-size distribution, and these products therefore generally have a high molasses number and comparatively low nitrogen BET and iodine numbers[18]. Such activated carbons are used mainly in applications that require the removal of large molecules from solutions, e.g. in the decolorization of sugar syrups. The absence of semiconductor properties in chemically activated carbons almost certainly relates to the fact that the temperature generally employed in the manufacture of these carbons is too low for the creation in the final product of graphitic zones, which are presumably responsible for the semiconductor–redox properties of thermally activated products[14,19].

The reduction potential of thermally activated carbons, measured[12] by a graphite-rod technique, has been found to be typically above −0,14 V versus the saturated calomel electrode at a pH value of 6. These carbons can therefore function as reducing agents, and many of the intriguing properties of thermally activated carbons, particularly their redox and catalytic properties, are believed to be related to their semiconductor properties.

It is interesting to note that chemically activated carbons have a poor affinity for the gold dicyanoaurate anion. This may be indicative of the important role played in the mechanism of gold extraction from a cyanide medium by the graphitic zones that are believed to exist in thermally activated carbon[14,20].

Since the high-temperature thermal route is employed most often for the manufacture of granular or shaped activated carbon products, and is also the most important route for the manufacture of products suitable for use in gold-recovery applications, that method will be focused on here. Furthermore, any detailed discussion of typical process routes for the preparation of activated carbon will be confined to those using coconut shells and coal as raw materials.

Process Route Using Coconut Shells

A typical flowsheet for the manufacture of activated carbon from presized or unsized char is depicted in Fig. 5. A similar route would be used for the manufacture of activated carbon from peach and apricot stones, or from any other hard, abrasion-resistant char, e.g. hard woods, which have sufficient inherent porosity to permit the activating agent to penetrate into the interior of the granule and simultaneously allow the products of the oxidation–gasification reactions to escape.

Details pertaining to the important unit operations that

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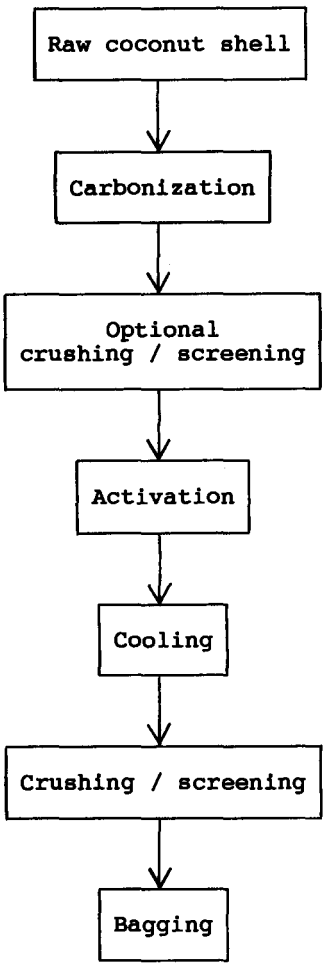

Fig. 5—Flowsheet for the manufacture of activated carbon from coconut-shell char (after Yehaskel[17])

constitute the process are discussed below.

Carbonization

A large quantity of coconut shells are available in countries such as the Philippines, Sri Lanka, and the South East Asian Islands as a byproduct of the coconut-oil and desiccated-coconut industries. Since coconut shells are eminently suitable for the production of very hard granular activated carbon, a viable industry for the manufacture of activated carbon has arisen in the Philippines and Sri Lanka. Because of its close proximity to the Philippines, Japan is a large importer of coconut-shell char and, hence, a manufacturer of activated coconut-shell carbon. As a matter of interest, the cigarette industry in Japan is the single largest consumer of activated coconut-shell carbon, since, in order to minimize the incidence of cancer due to smoking, the law requires fine carbon granules to be used in cigarette filters to adsorb the volatile organic materials emanating from the burning tobacco.

In the coconut-shell industry, carbonization is generally a small-scale, primitive, and crude operation that is conducted in the heart of the coconut plantations by individual farmers in, for example, 200-litre drums cut in half. Copra is placed in the bottom of the drum, which is then filled with coconut shells and ignited. The drum is covered with a sheet of metal, and the coconut shells are allowed to char for a couple of hours in an atmosphere that is essentially depleted of air. The char is sold to central depots, usually established by the various local manufacturers or exporters of char. Although charring is also sometimes done on a larger scale in pits, or simply in trenches dug in the sand on beaches, it is very much a cottage industry. Quality control in relation to char is conducted on the premises of the manufacturer using various techniques based on density separation.

As was mentioned earlier, carbonization is essentially a devolatilization step, which produces a char with a significantly higher content of fixed carbon (between 70 and 85 per cent) than is present in raw coconut shells.

Activation

Prior to activation, the carbonized material may be crushed, sized, and freed from extraneous materials such as sand, or large chunks of it may be fed directly to the activation stage. Activation is usually conducted in a directly fired rotary kiln, where the product is activated at between 800 and 1000°C in the presence of steam, air, flue gas, or mixtures of these, for a period of time.

The development of a highly porous product is generally associated with the degree of burn-off or loss in mass of the char, i.e. the extent to which the gasification reactions shown in equations (2) and (3) have been allowed to proceed.

In the activation of carbonaceous materials, there are at least five primary variables that can affect the surface area and pore-size distribution of the product and, hence, its adsorptive properties:

(1) the nature of the starting material or quality of the char,
(2) the composition of the activation atmosphere,
(3) the flowrate of the activating gases,
(4) the temperature of activation, and
(5) the duration of the burn-off period.

The interrelationship between the various activation parameters is complex, and therefore the qualitative representations given in Figs. 6 to 8 are only simplistic qualitative representations. The data presented, which are not accurate, serve only to indicate relative trends, and are equally applicable to any type of carbonaceous raw material.

The nature of the source material has a marked effect on certain properties of the final product, e.g. the pore-size distribution and hardness, as will be discussed in greater detail later. The composition of the activation atmosphere is most important, not only in terms of the reactions referred to earlier, but because of its effect on the nature of the surface oxides that form in the carbon during activation. This affects the hydrophobic/hydrophilic balance and, hence, the adsorptive behaviour and selectivity trends of the product.

Fig. 6 indicates that the yield of final product, which is inversely proportional to the extent of burn-off, decreases as the residence time in the kiln is increased, and is also markedly dependent on the temperature of activation, which obviously affects the rate of burn-off or gasification.

The activity of the product as measured by nitrogen BET adsorption is approximately proportional to the degree of burn-off up to a certain point, as is apparent from Fig. 7, and corresponds to the formation of microporosity in the product. However, a point is reached

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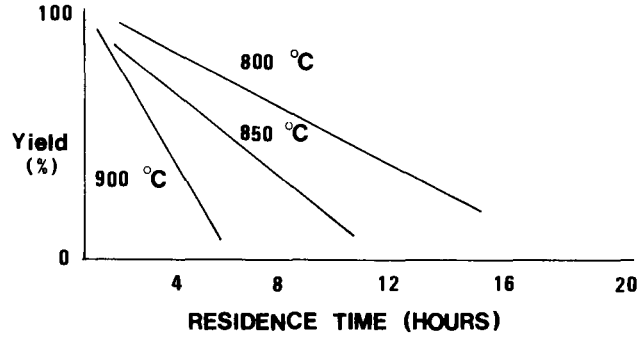

Fig. 6—Qualitative relationship between yield of activated carbon and residence time in the kiln at various temperatures

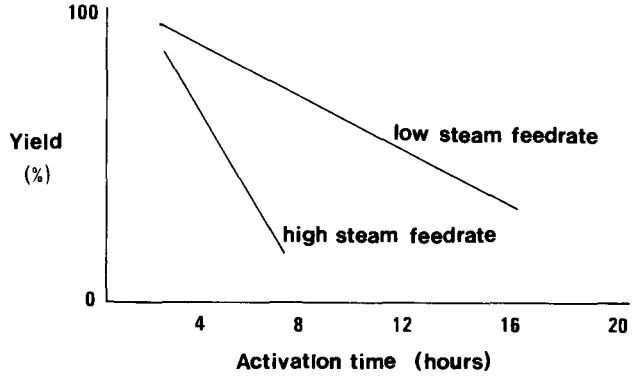

Fig. 8—Qualitative relationship between yield of activated carbon and residence time in the kiln at high and low feed rates of steam

where further burn-off results in a reduction in the nitrogen BET surface, and this phenomenon relates to the conversion of micropores into mesopores and macropores by the burning-away of the pore walls. There is usually a concomitant loss in the structural strength of the product.

Fig. 8 depicts the relationship between yield and residence time in the kiln as a function of the steam feed rate. In this case, it is apparent that higher steam feed rates enhance the rate of burn-off, thereby decreasing the yield of final product.

Once the desired level of activity has been achieved, the product is cooled to below the ignition point of carbon in air (usually less than 400°C), and bagged directly or after further crushing and sizing.

Because of the adsorptive properties of activated carbon, it is important that the product should be sealed from the atmosphere. Activated carbon is therefore usually packed directly into polyethylene bags and sealed before being placed in a second, stronger bag made of a material such as woven polypropylene.

Characteristics of Activated Coconut-shell Carbon

One of the most important characteristics of activated carbon made from coconut shells is that it is extremely microporous, the major portion of its pore volume being represented by pores with a radius of 10 Å, as can be seen from the pore-size distribution curve shown in Fig. 9. For comparative purposes, a curve of typical pore-size distribution for a chemically activated wood carbon is also shown; this curve indicates the presence of a high content of mesopores and macropores.

For this reason, coconut-shell products are ideal for the adsorption of small gaseous molecules that fit snugly

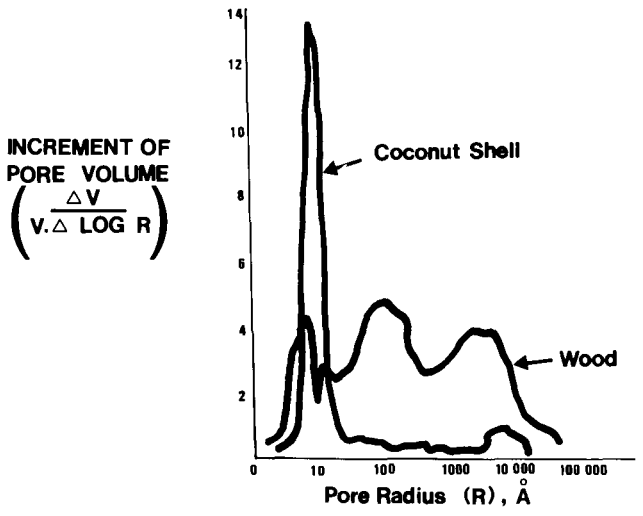

Fig. 9—Pore-size distributions in typical thermally activated coconut-shell carbon and chemically activated wood carbon

into the micropores, and are therefore extensively employed in gas-phase and solvent-recovery applications in general[6,8,10]. However, coconut-shell products generally fare poorly in applications involving the treatment of industrial effluents because the molecules that have to be adsorbed are often too large to penetrate into the microporous carbon matrix, and are therefore adsorbed less efficiently.

The extremely good impact hardness and wet abrasion resistance of coconut-shell carbons, combined with their

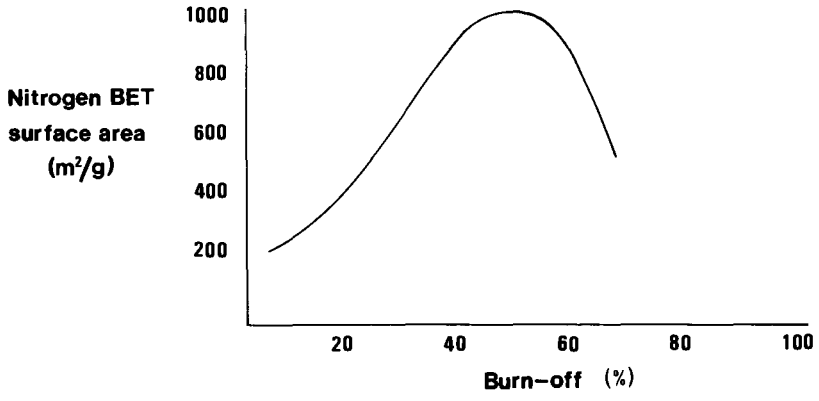

Fig. 7—Qualitative relationship between nitrogen BET surface area and loss in mass of char during activation

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high adsorptive capacity for the small gold-dicyanoaurate complex, makes these carbons ideal for applications involving gold recovery, particularly in carbon-in-pulp (CIP) and carbon-in-leach (CIL) processes.

The nature of the surface oxides formed in the carbon, and the activity of the product as measured, for instance, by the extent to which selected molecules from the gaseous or aqueous phase are adsorbed, are determined by the activation parameters, but the structure of the pores and the pore-size distribution are predetermined to a large extent by the source material[10,16]. This is apparent from photomicrographs of the pore structure of activated carbons manufactured from coconut shells and peach pips, and indicates that the structure of the original source material, viz the cellular structure of the coconut shell and the peach pips, is still present in the carbon skeleton of the final product[8].

Therefore, the inherent cellular structure of raw materials of vegetable origin imposes a constraint on the degree to which the properties of the product can be modified for special applications. For example, the micropores of the cellular structure of coconut shell can be converted into macropores by burning-away of the cell walls, thus changing the adsorption properties of the final product. Unfortunately, this type of modification is accompanied by a loss in the structural integrity and, hence, the strength of the product, as well as a decrease in product yield.

Process Routes Using Coal

Fig. 10 illustrates the various unit operations that are generally involved in the manufacture of granular activated carbons from coal[17].

Process routes using coal as the starting material are significantly more complex than those generally employed in the manufacture of coconut-shell carbons, as is indicated by the large number of unit operations involved.

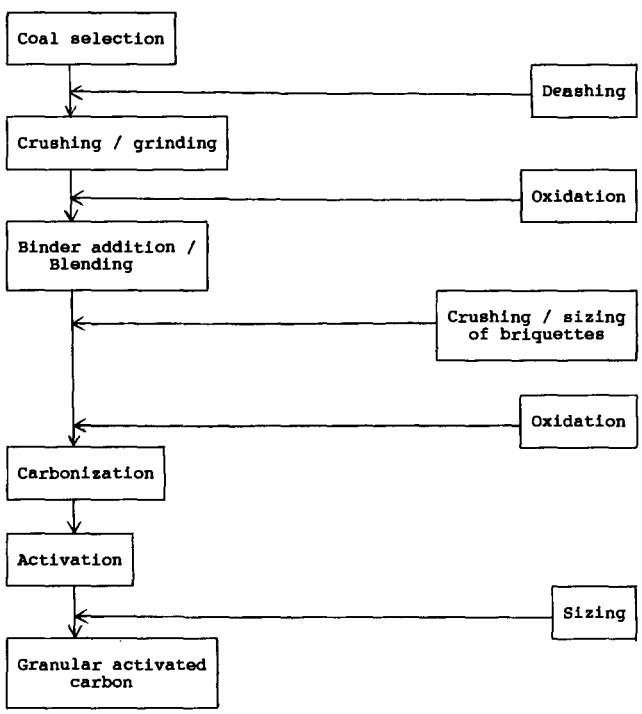

Fig. 10—Flowsheet showing the unit operations that are generally involved in the manufacture of granular activated carbons from coal (after Yehaskel[17])

Owing to the wide availability of abundant quantities of coal, particularly in the Western World, some of the largest commercial production facilities are based on coal as a raw material. However, the particular processing route employed depends mainly on the nature of the coal and the form in which the product is required (crushed or extruded), and hundreds of patents have been registered to describe the numerous process routes developed over the years for the manufacture of granular carbons from various ranks of coal (peat, brown coal, bituminous coal, lignite, coking coal, and anthracite)[17].

A low ash content is one of the most important requirements of a coal that is used for activated carbon. The major reasons for this relate to the fact that the ash content may catalyse certain undesirable activation effects, and is also believed to adversely affect the strength of the final product. Therefore, with high-ash coals, deashing with mineral acid may be necessary. The details of the other unit operations are discussed in the following sections.

Crushing, Grinding, and Oxidation

The inherent porosity of most ranks of coal is very low, and therefore the coal used as a starting material requires pretreatment to increase its porosity. The coal is initially crushed and milled by conventional means into a fine powder, after which it is reconstituted by briquetting or extrusion with the aid of a coking binder such as coal-tar pitch. This procedure may result in up to a tenfold increase in porosity over that of the coal as received from the mine. This porosity allows for uniform gasification of the coal granules during activation by providing channels that permit the oxidizing gases to enter the particle, while allowing the reaction products to escape.

Oxidation of the coal, either as a powder or after granulation, is often an important intermediate stage, depending on the nature of the coal. For example, the agglomerating property of a high-rank medium-volatile bituminous coal is destroyed if the coal is oxidized at a temperature below its fusion point, i.e. between 200 and 280°C. This treatment alters organic components in the coal, thereby rendering the particles non-agglomerative, and can be conducted either in a fluidized bed (coal powder) or in a rotary kiln (granules). The average residence time for oxidation varies between 10 minutes and 1 hour. Careful temperature control is critical because, above about 375°C, the characteristic particle shape is destroyed, and the particles may fuse. Steam is often injected into the kiln for purposes of temperature control.

Briquetting and Extrusion

Granular activated carbons can be crushed or pressed. The products of crushed granular coal are produced by briquetting, the briquette being crushed and sized prior to oxidation or carbonization, or only after activation. The particle-size range is usually between 0,2 and 3,5 mm.

The second type of granular carbon, viz pressed or extruded carbon, is usually produced in uniform cylindrical shapes. These are always formed prior to carbonization and activation. In the process, the coal powder

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is blended with a coking binder, usually coal-tar pitch, although numerous other types of binders are also employed commercially, at a temperature above the softening point of the pitch. The resultant plastic mass is then extruded from a die, and the rod is cut into pieces of uniform length. The diameter of the cylinders usually varies between 0,8 and 4,0 mm, and the length is from one to three times greater than the diameter.

Carbonization and Activation

General aspects related to carbonization and activation are no different from those discussed previously for coconut shells, and are therefore not repeated here.

Characteristics of Coal-based Activated Carbons

Coal-based activated-carbon products are characterized by a tridisperse pore-size distribution, i.e. they contain micropores, mesopores, and macropores, as is apparent from Fig. 11. For this reason, they constitute a very versatile range of products and are generally employed in a wide variety of aqueous-phase applications requiring the removal of a range of molecules varying significantly in molecular size, e.g. in the treatment of effluent water.

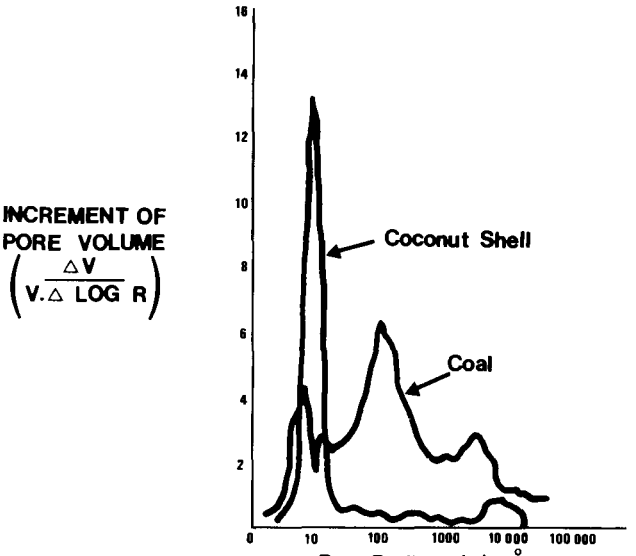

Fig. 11—Pore-size distributions for a typical thermally activated coal-based carbon and a coconut-shell carbon (after Fornwalt *et al*[18])

When cognizance is taken of the many variables involved in the manufacture of coal-based products (the rank of the coal, the binder chosen, the briquetting or extrusion technology used, the combination of activation parameters chosen, the fineness of grind employed, etc.), it is obvious that the scope for modification of the product is significant. For example, coal-based products cannot be modified to simulate the properties of coconut-shell or wood-based products, although any modifications between these extremes are possible.

It is also generally accepted that the abrasion resistance and impact hardness of these reconstituted products, based on current manufacturing technology, is with few exceptions not as good as those found in products using coconut shells as the raw material.

Selection of an Activated Carbon for Gold Recovery

The primary requisites[19] for a granular activated carbon intended for use in gold-recovery applications are as follows:

(a) the carbon must have a high gold activity, and
(b) the carbon must be tough and resistant to abrasion, for this will minimize the loss of gold associated with fine abraded carbon in the tailings.

Since activated carbons manufactured from coconut shells best meet the above requirements, they are widely employed in gold-recovery applications. Other important parameters relate to particle size (the rate of gold extraction increases with decreasing particle size), the initial and equilibrium gold concentrations, the surface area of the product, the pH value and temperature of the adsorption medium, etc.[12,13,19].

Conclusions

The main objective in the manufacture of granular activated carbon is the development of an optimum pore structure associated with a high surface area—with minimum loss of the carbon content through carbonization and oxidation—and of a product with sufficient structural strength to withstand normal usage without excessive attrition of the particles.

The manufacture of high-quality activated-carbon products is significantly more complex than has been outlined here because of the number of variables involved in the manufacturing process, and the complex interrelationship between those variables. As discussed, when unsophisticated methods of manufacture are employed, each raw material tends to produce its own characteristic type of pore structure. Nevertheless, this natural tendency can be altered considerably by special treatment requiring considerable effort and know-how.

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Mine valuation and grade control

The South African Institute of Mining and Metallurgy will be holding a 2-day school on 6th and 7th June, 1991, on the topic **Mine Valuation and Grade Control.**

Objective

The objective of this School is to present the practical application of valuation and grade control as they apply to the accounting for metal and grade of broken ore from the *in situ* to the final saleable product.

The latest developments in this field relating to the mining of precious metals, coal, and base minerals will be covered.

Programme

Sessions will be held on the following topics:

- Reserves (Chairman: Dr I. Clark)
- Dilution (Chairman: Dr G.A. Fourie)
- Mineral Flow (Chairman: Mr L.V. Estment)
- Stockpiling (Chairman: Mr N. de Wet)
- Plant (Chairman: Mr J. Shirley)
- Quality Control (Chairman: Mr D.J. van Niekerk).

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Telex: 4-86431.

Mine productivity and safety

The South African Institute of Mining and Metallurgy will be holding a one-day colloquium devoted to **Communications and Monitoring to Improve Mine Productivity and Safety.**

This Colloquium will cover a range of topics dealing with the following systems planned or in operation in underground and surface mines:

- Voice communications and telemetry underground
- Rock and personnel tracking
- Environmental monitoring and alarm
- Rope-load monitoring
- Equipment-condition monitoring
- Shaft management.

The Colloquium will be held on 21st May, 1991, at the BIFSA Conference Centre, Halfway House, Midrand.

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Bacterial oxidation

The South African Institute of Mining and Metallurgy will be holding a colloquium on **Bacterial Oxidation** in June 1991 in Johannesburg.

The papers will be published in a bound volume, which will be available to all delegates on registration at the Colloquium. The language of the Colloquium will be English.

The final circular will contain detailed information on the Colloquium, as well as the registration forms.

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