CARBON, ACTIVATED

1. Introduction

Activated carbon is a predominantly amorphous solid that has an extraordinarily large internal surface area and pore volume. These unique characteristics are responsible for its adsorptive properties, which are exploited in many different liquid- and gas-phase applications. Activated carbon is an exceptionally versatile adsorbent because the size and distribution of the pores within the carbon matrix can be controlled to meet the needs of current and emerging markets (1). Engineering requirements of specific applications are satisfied by producing activated carbons in the form of powders, granules, and shaped products. Through choice of precursor, method of activation, and control of processing conditions, the adsorptive properties of products are tailored for applications as diverse as the purification of potable water and the control of gasoline emissions from motor vehicles.

In 1900, two very significant processes in the development and manufacture of activated carbon products were patented (2). The first commercial products were produced in Europe under these patents: Eponite, from wood in 1909, and Norit, from peat in 1911. Activated carbon was first produced in the United States in 1913 by Westvaco Corp. under the name Filtchar, using a by-product of the papermaking process (3). Further milestones in development were reached as a result of World War I. In response to the need for protective gas masks, a hard, granular activated carbon was produced from coconut shell in 1915. Following the war, large-scale commercial use of activated carbon was extended to refining of beet sugar and corn syrup and to purification of municipal water supplies (4). The termination of the supply of coconut char from the Philippines and India during World War II forced the domestic development of granular activated carbon products from coal in 1940 (5). More recent innovations in the manufacture and use of activated carbon products have been driven by the need to recycle resources and to prevent environmental pollution.

2. Physical and Chemical Properties

The structure of activated carbon is best described as a twisted network of defective carbon layer planes, cross-linked by aliphatic bridging groups (6). X-ray diffraction patterns of activated carbon reveal that it is nongraphitic, remaining amorphous because the randomly cross-linked network inhibits reordering of the structure even when heated to 3000°C (7). This property of activated carbon contributes to its most unique feature, namely, the highly developed and accessible internal pore structure. The surface area, dimensions, and distribution of the pores depend on the precursor and on the conditions of carbonization and activation. Pore sizes are classified (8) by the International Union of Pure and Applied Chemistry (IUPAC) as micropores (pore width <2 nm), mesopores (pore width 2–50 nm), and macropores (pore width >50 nm) (see ADSORPTION).

The surface area of activated carbon is usually determined by application of the Brunauer-Emmett-Teller (BET) model of physical adsorption (9,10) using nitrogen as the adsorptive (8). Typical commercial products have specific surface areas in the range 500–2000 m^2/g, but values as high as 3500–5000 m^2/g have been reported for some activated carbons (11,12). In general, however, the effective surface area of a microporous activated carbon is far smaller because the adsorption of nitrogen in micropores does not occur according to the process assumed in the BET model, which results in unrealistically high values for surface area (10,13). Adsorption isotherms are usually determined for the appropriate adsorptives to assess the effective surface area of a product in a specific application. Adsorption capacity and rate of adsorption depend on the internal surface area and distribution of pore size and shape but are also influenced by the surface chemistry of the activated carbon (14). The macroporosity of the carbon is important for the transfer of adsorbate molecules to adsorption sites within the particle.

Functional groups are formed during activation by interaction of free radicals on the carbon surface with atoms such as oxygen and nitrogen, both from within the precursor and from the atmosphere (15). The functional groups render the surface of activated carbon chemically reactive and influence its adsorptive properties (6). Activated carbon is generally considered to exhibit a low affinity for water, which is an important property with respect to the adsorption of gases in the presence of moisture (16). However, the functional groups on the carbon surface can interact with water, rendering the carbon surface more hydrophilic (15). Surface oxidation, which is an inherent feature of activated carbon production, results in hydroxyl, carbonyl, and carboxylic groups that impart an amphoteric character to the carbon, so that it can be either acidic or basic. The electrokinetic properties of an activated carbon product are, therefore, important with respect to its use as a catalyst support (17). As well as influencing the adsorption of many molecules, surface oxide groups contribute to the reactivity of activated carbons toward certain solvents in solvent recovery applications (18).

In addition to surface area, pore size distribution, and surface chemistry, other important properties of commercial activated carbon products include pore volume, particle size distribution, apparent or bulk density, particle density, abrasion resistance, hardness, and ash content. The range of these and other properties is illustrated in Table 1 together with specific values for selected commercial grades of powdered, granular, and shaped activated carbon products used in liquid- or gas-phase applications (19).

Table 1. **Properties of Selected U.S. Activated Carbon Products**[a]

Property	Manufacturer Precursor Product grade Product form Typical range	Gas-phase carbons			Liquid-phase carbons		
		Calgon Coal BPL Granular	Norit Peat B4 Extruded	Westvaco Wood WV-A 1100 Granular	Calgon Coal SGL Granular	Norit Peat SA 3 Powdered	Westvaco Wood SA-20 Powdered
particle size, U.S. mesh[b,c]	<4	12 × 30	3.8 mm	10 × 25	8 × 30	64%	65 − 85%
apparent density, g/cm^3	0.2–0.6	>0.48	0.43	0.27	0.52	0.46	0.34–0.37
particle density, g/cm^3	0.4–0.9	0.80		0.50	0.80		
hardness number	50–100	>90	99				
abrasion number					>75		
ash, wt %	1–20		6			6	3–5
BET surface area, N_2, m^2/g	500–2500	1050–1150	1100–1200	1750	900–1000	750	1400–1800
total pore volume, cm^3/g	0.5–2.5	0.8	0.9	1.2	0.85		2.2–2.5
CCl_4 activity, wt %	35–125	>60					
butane working capacity, g/100 cm^3	4–14			>11.0			
iodine number	500–1200	>1050			>900	800	>1000
decolorizing index							
Westvaco	15–25						>20
molasses number							
Calgon	50–250				>200		
Norit	300–1500					440	
heat capacity at 100°C, J/(g · K)[d]	0.84–1.3	1.05			1.05		
thermal conductivity, W/(m · K)	0.05–0.10						

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[a] Specific values shown are those cited in manufacturers' product literature (19). Typical ranges shown are based on values reported in the open literature.

[b] Unless otherwise noted.

[c] Approximate mm corresponding to cited meshes are mesh: mm—4: 4.76; 8: 2.38; 10: 2; 12: 1.68; 25: 0.72; 30: 0.59; 325: 0.04.

[d] To convert J to cal, divide by 4.184.

3. Manufacture and Processing

Commercial activated carbon products are produced from organic materials that are rich in carbon, particularly coal, lignite, wood, nut shells, peat, pitches, and cokes. The choice of precursor is largely dependent on its availability, cost, and purity, but the manufacturing process and intended application of the product are also important considerations. Manufacturing processes fall into two categories, thermal activation and chemical activation. The effective porosity of activated carbon produced by thermal activation is the result of gasification of the carbon at relatively high temperatures (20), but the porosity of chemically activated products is generally created by chemical dehydration reactions occurring at significantly lower temperatures (1,21).

3.1. Thermal Activation Processes. Thermal activation occurs in two stages: thermal decomposition or carbonization of the precursor and controlled gasification or activation of the crude char. During carbonization, elements such as hydrogen and oxygen are eliminated from the precursor to produce a carbon skeleton possessing a latent pore structure. During gasification, the char is exposed to an oxidizing atmosphere that greatly increases the pore volume and surface area of the product through elimination of volatile pyrolysis products and from carbon burn-off. Carbonization and activation of the char are generally carried out in direct-fired rotary kilns or multiple hearth furnaces, but fluidized-bed reactors have also been used (22). Materials of construction, notably steel and refractories, are designed to withstand the high temperature conditions, ie, $>1000°C$, inherent in activation processes. The thermal activation process is illustrated in Figure 1 for the production of activated carbon from bituminous coal (23,24).

Bituminous coal is pulverized and passed to a briquette press. Binders may be added at this stage before compression of the coal into briquettes. The briquetted coal is then crushed and passed through a screen, from which the on-size material passes to an oxidizing kiln. Here, the coking properties of the coal particles are destroyed by oxidation at moderate temperatures in air. The oxidized coal is then devolatilized in a second rotary kiln at higher temperatures under steam. To comply with environmental pollution regulations, the kiln off-gases containing dust and volatile matter pass through an incinerator before discharge to the atmosphere.

The devolatilized coal particles are transported to a direct-fired multihearth furnace where they are activated by holding the temperature of the furnace at about 1000°C. Product quality is maintained by controlling coal feed rate and bed temperature. As before, dust particles in the furnace off-gas are combusted in an afterburner before discharge of the gas to the atmosphere. Finally, the granular product is screened to provide the desired particle size. A typical yield of activated carbon is about 30–35% by weight based on the raw coal.

The process for the thermal activation of other carbonaceous materials is modified according to the precursor. For example, the production of activated carbon from coconut shell does not require the stages involving briquetting, oxidation, and devolatilization. To obtain a high activity product, however, it is important that the coconut shell is charred slowly prior to activation of the

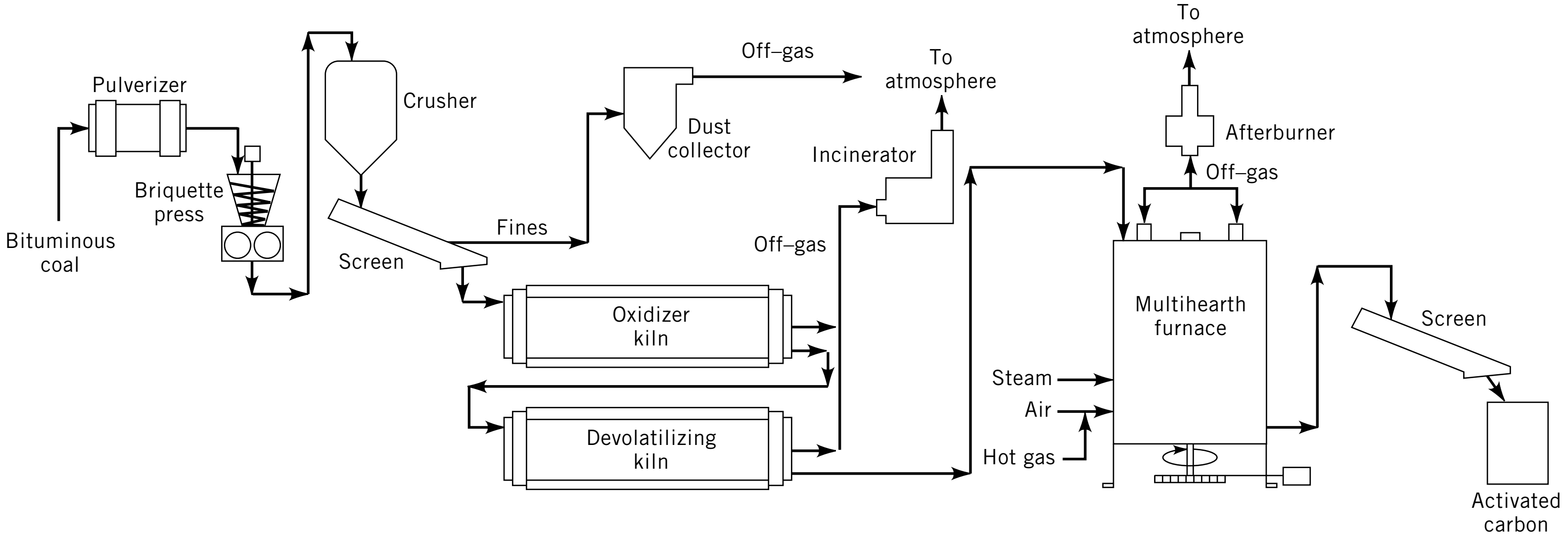

Fig. 1. Thermal activation of bituminous coal.

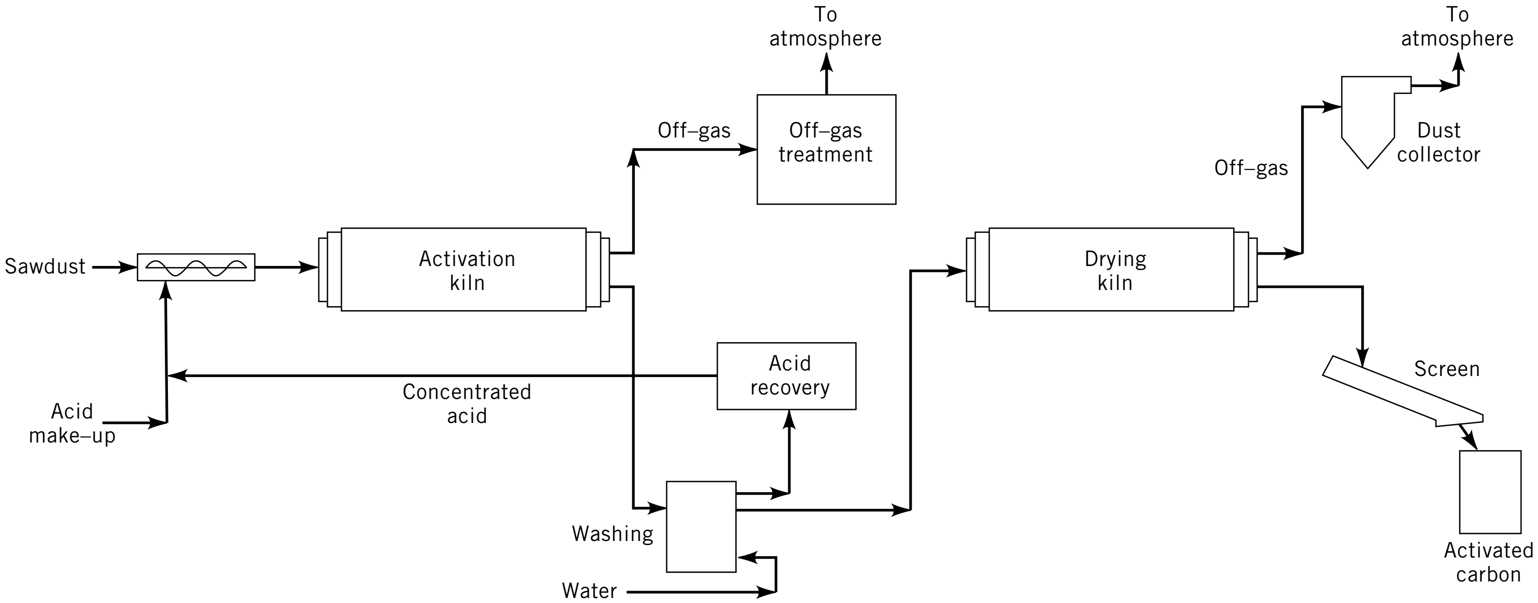

Fig. 2. Chemical activation of wood.

char. In some processes, the precursor or product is acid-washed to obtain a final product with a low ash content (23,25).

3.2. Chemical Activation Processes.

In contrast to the thermal activation of coal, chemical activation is generally carried out commercially in a single kiln. The precursor, usually wood, is impregnated with a chemical activation agent, typically phosphoric acid, and the blend is heated to a temperature of 450–700°C (26). Chemical activation agents reduce the formation of tar and other by-products, thereby increasing carbon yield. The chemical activation process is illustrated in Figure 2, for the production of granular activated carbon from wood (23,27).

Sawdust is impregnated with concentrated phosphoric acid and fed to a rotary kiln, where it is dried, carbonized, and activated at a moderate temperature. To comply with environmental pollution regulations, the kiln off-gases are treated before discharge to the atmosphere. The char is washed with water to remove the acid from the carbon, and the carbon is separated from the slurry. The filtrate is then passed to an acid recovery unit. Some manufacturing plants do not recycle all the acid but use a part of it to manufacture fertilizer in an allied plant. If necessary, the pH of the activated carbon is adjusted, and the product is dried. The dry product is screened and classified into the size range required for specific granular carbon applications. Carbon yields as high as 50% by weight of the wood precursor have been reported (26).

Other Manufacturing Processes. Different chemical activation processes have been used to produce carbons with enhanced adsorption characteristics. Activated carbons of exceptionally high surface area (>3000 m^2/g) have been produced by the chemical activation of carbonaceous materials with potassium hydroxide (28,29). Activated carbons are also produced commercially in the form of cloths (30), fibers (31), and foams (32) generally by chemical activation of the precursor with a Lewis acid such as aluminum chloride, ferric chloride, or zinc chloride.

3.3. Forms of Activated Carbon Products.

To meet the engineering requirements of specific applications, activated carbons are produced and classified as granular, powdered, or shaped products. Granular activated carbons are produced directly from granular precursors, such as sawdust and crushed and sized coconut char or coal. The granular product is screened and sized for specific applications. Powdered activated carbons are obtained by grinding granular products. Shaped activated carbon products are generally produced as cylindrical pellets by extrusion of the precursor with a suitable binder before activation of the precursor.

4. Shipment and Storage

Activated carbon products are shipped in bags, drums, and boxes in weights ranging from about 10 to 35 kg. Containers can be lined or covered with plastic and should be stored in a protected area both to prevent weather damage and to minimize contact with organic vapors that could reduce the adsorption performance of the product. Bulk quantities of activated carbon products are shipped in metal bins and bulk bags, typically 1–2 m^3 in volume, and in railcars and tank

Table 2. **U.S. Producers of Activated Carbon and Their Capacities**[a]

Producer	Capacity, × 10^6 kg	(× 10^6 lb)
Barnebey & Sutcliffe, Columbus, Ohio	13.6	(30)
Calgon Carbon, Catlettsburg, Ky.	63.5	(140)
Calgon Carbon, Pearlington, Miss.	18.1	(40)
Norit Americas, Pryor, Okla.	15.8	(35)
Norit Americas, Marshall, Texas	45.3	(100)
Royal Oak, Romeo, Fla.	9.1	(20)
Westvaco, Covington, Va.	22.7	(50)
Westvaco, Wickliffe, Ky.	22.7	(50)
Total	*210.8*	(465)

[a] From Ref. 33.

trucks. Bulk carbon shipments are generally transferred by pneumatic conveyors and stored in tanks. However, in applications such as water treatment where water adsorption does not impact product performance, bulk carbon may be transferred and stored as a slurry in water.

5. Economic Aspects

U.S. producers of activated carbon are listed in Table 2.

Demand in 1999 was 168 × 10^6 kg (370 × 10^6 lb); in 2000 it was 173 × 10^6 kg (381 × 10^6 lb). The forecast for 2004 is 206 × 10^6 kg (454 × 10^6 lb). Demand equals production plus imports less exports. Imports in 2000 totaled 49 × 10^6 kg (109 × 10^6 lb) (33).

Growth is expected at the rate of 4.5% through 2004. Demand is driven by environmental considerations. In many applications, adtivated carbon has best available technology status. However, some alternative systems may be more cost effective (33).

Price history for the years 1995–2000 was a high of \$0.50/kg (\$1.10/lb) gran. and a low of \$0.20/kg (\$0.45/lb) (33).

6. Specifications

Activated carbon producers furnish product bulletins that list specifications, usually expressed as a maximum or minimum value, and typical properties for each grade produced. Standards helpful in setting purchasing specifications for granular and powdered activated carbon products have been published (34,35).

7. Analytical Test Procedures and Standards

Source references for frequently used test procedures for determining properties of activated carbon are shown in Table 3. A primary source is the *Annual Book of*

Table 3. **Source References for Activated Carbon Test Procedures and Standards**

Title of procedure or standard	Source
Standard Definitions of Terms Relating to Activated Carbon	ASTM D2652
Apparent Density of Activated Carbon	ASTM D2854
Particle Size Distribution of Granular Activated Carbon	ASTM D2862
Total Ash Content of Activated Carbon	ASTM D2866
Moisture in Activated Carbon	ASTM D2867
Ignition Temperature of Granular Activated Carbon	ASTM D3466
Carbon Tetrachloride Activity of Activated Carbon	ASTM D3467
Ball-Pan Hardness of Activated Carbon	ASTM D3802
Radioiodine Testing of Nuclear-Grade Gas-Phase Adsorbents	ASTM D3803
pH of Activated Carbon	ASTM D3838
Determination of Adsorptive Capacity of Carbon by Isotherm Technique	ASTM D3860
Determining Operating Performance of Granular Activated Carbon	ASTM D3922
Impregnated Activated Carbon Used to Remove Gaseous Radio-Iodines from Gas Streams	ASTM D4069
Determination of Iodine Number of Activated Carbon	ASTM D4607
Military Specification, Charcoal, Activated, Impregnated	Ref. 36
Military Specification, Charcoal, Activated, Unimpregnated	Ref. 36
AWWA Standard for Granular Activated Carbon	Ref. 34
AWWA Standard for Powdered Activated Carbon	Ref. 35
BET Surface Area by Nitrogen Adsorption	Refs. 6,8,9,37
Pore Volume by Nitrogen Adsorption or Mercury Penetration	Refs. 10,38–40
Particle Density	Ref. 41

American Society for Testing and Materials (ASTM) Standards (42). Other useful sources of standards and test procedures include manufacturers of activated carbon products, the American Water Works Association (AWWA) (34,35), and the Department of Defense (36).

8. Health and Safety Factors

Activated carbon generally presents no particular health hazard as defined by NIOSH (43). However, it is a nuisance and mild irritant with respect to inhalation, skin contact, eye exposure, and ingestion. On the other hand, special consideration must be given to the handling of spent carbon that may contain a concentration of toxic compounds.

Activated carbon products used for decolorizing food products in liquid form must meet the requirements of the *Food Chemical Codex* as prepared by the Food & Nutrition Board of the National Research Council (44).

According to the National Board of Fire Underwriters, activated carbons normally used for water treatment pose no dust explosion hazard and are not subject to spontaneous combustion when confined to bags, drums, or storage bins (45). However, activated carbon burns when sufficient heat is applied; the ignition point varies between about 300 and 600°C (46).

Dust-tight electrical systems should be used in areas where activated carbon is present, particularly powdered products (47). When partially wet activated carbon comes into contact with unprotected metal, galvanic currents can be set up; these result in metal corrosion (48).

Manufacturer material safety data sheets (MSDS) indicate that the oxygen concentration in bulk storage bins or other enclosed vessels can be reduced by wet activated carbon to a level that will not support life. Therefore, self-contained air packs should be used by personnel entering enclosed vessels where activated carbon is present (49).

9. Environmental Concerns

Activated carbon is a recyclable material that can be regenerated. Thus the economics, especially the market growth, of activated carbon, particularly granular and shaped products, is affected by regeneration and industry regeneration capacity. The decision to regenerate an activated carbon product is dependent on the cost, size of the carbon system, type of adsorbate, and the environmental issues involved. Large carbon systems, such as those used in potable and wastewater treatment, generally require a high temperature treatment, which is typically carried out in rotary or multihearth furnaces. During regeneration, carbon losses of 1 to 15% typically occur from the treatment and movement of the carbon (50). However, material loss is compensated for by the addition of new carbon to the adsorber system. In general, regeneration of spent carbon is considerably less expensive than the purchase of new activated carbon. For example, fluidized-bed furnace regeneration of activated carbon used in a 94,600 m^3 per day water treatment system cost only 35% of new material (51). For this system, regeneration using either infrared or multihearth furnaces was estimated to be more expensive but still significantly less so than the cost of new carbon.

Because powdered activated carbon is generally used in relatively small quantities, the spent carbon has often been disposed of in landfills. However, landfill disposal is becoming more restrictive environmentally and more costly. Thus large consumers of powdered carbon find that regeneration is an attractive alternative. Examples of regeneration systems for powdered activated carbon include the Zimpro/Passavant wet air oxidation process (52), the multihearth furnace as used in the DuPont PACT process (53,54), and the Shirco infrared furnace (55,56).

Other types of regenerators designed for specific adsorption systems may use solvents and chemicals to remove susceptible adsorbates (57), steam or heated inert gas to recover volatile organic solvents (58), and biological systems in which organics adsorbed on the activated carbon during water treatment are continuously degraded (59).

10. Liquid-Phase Applications

Liquid phase applications account for 82% of total activated carbon. They include potable water, 31%; industrial and municipal wastewater, 22%; sweetener decolorization, 11%; groundwater, 9%; household uses, 6%; food and beverages, 5%; mining, 4%; pharmaceuticals, 3%; miscellaneous, including chemical processing, 9% (33). Activated carbons for use in liquid-phase applications differ from gas-phase carbons primarily in pore size distribution. Liquid-phase carbons have significantly more pore volume in the macropore range, which permits liquids to diffuse more rapidly into the mesopores and micropores (60). The larger pores also promote greater adsorption of large molecules, either impurities or products, in many liquid-phase applications. Specific-grade choice is based on the isotherm (61,62) and, in some cases, bench or pilot scale evaluations of candidate carbons.

Liquid-phase activated carbon can be applied either as a powder, granular, or shaped form. The average size of powdered carbon particles is 15–25 μm (61). Granular or shaped carbon particle size is usually 0.3–3.0 mm. A significant factor in choosing between powdered and nonpowdered carbon is the degree of purification required in the adsorption application. Granular and shaped carbons are usually used in continuous flow through deep beds to remove essentially all contaminants from the liquid being treated. Granular and shaped carbon systems are preferred when a large carbon buffer is needed to withstand significant variations in adsorption conditions, such as in cases where large contaminant spikes may occur. A wider range of impurity removal can be attained by batch application of powdered carbon, and the powdered carbon dose per batch can be controlled to achieve the degree of purification desired (60) (see ADSORPTION, LIQUID SEPARATION).

Batch-stirred vessels are most often used in treating material with powdered activated carbon (63). The type of carbon, contact time, and amount of carbon vary with the desired degree of purification. The efficiency of activated carbon may be improved by applying continuous, countercurrent carbon–liquid flow with multiple stages (Fig. 3). Carbon is separated from the liquid at each stage by settling or filtration. Filter aids such as diatomaceous earth are sometimes used to improve filtration.

Granular and shaped carbons are used generally in continuous systems where the liquid to be treated is passed through a fixed bed (63,64). New binder technology produces shaped carbon bodies having key properties beyond the best level that has been accomplished with other binders (65). Compounds are

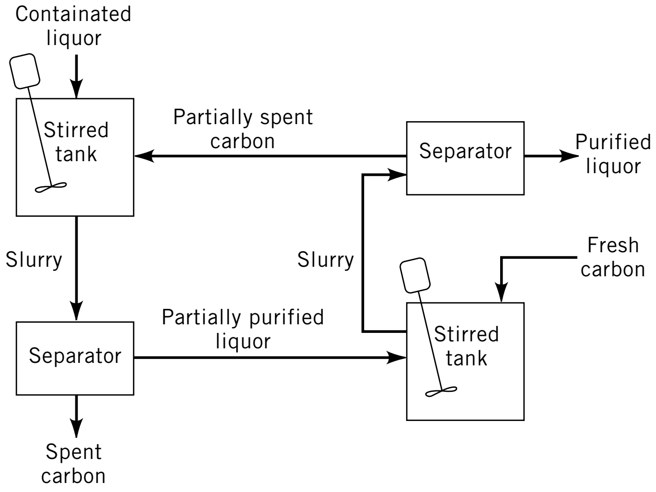

Fig. 3. Multistage countercurrent application of powdered activated carbon.

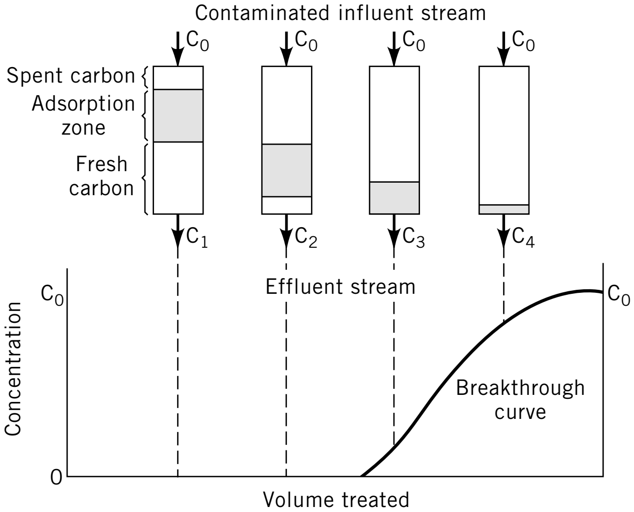

Fig. 4. Adsorption zone and breakthrough curve for fixed bed of granular or shaped activated carbon.

adsorbed by the carbon bed in the adsorption zone (Fig. 4). As carbon in the bed becomes saturated with adsorbates, the adsorption zone moves in the direction of flow, and breakthrough occurs when the leading edge of the adsorption zone reaches the end of the column. Normally at least two columns in series are on line at any given time. When the first column becomes saturated, it is removed from service, and a column containing fresh carbon is added at the discharge end of the series. An alternative approach is the moving bed column (64). In this design the adsorption zone is contained within a single column by passing liquid upward while continuously or intermittently withdrawing spent carbon at the bottom and adding fresh carbon at the top.

10.1. Potable Water Treatment. Treatment of drinking water accounts for about 31% of the total activated carbon used in liquid-phase applications (33). Rivers, lakes, and groundwater from wells, the most common drinking water sources, are often contaminated with bacteria, viruses, natural vegetation decay products, halogenated materials, and volatile organic compounds. Normal water disinfection and filtration treatment steps remove or destroy the bulk of these materials (66). However, treatment by activated carbon is an important additional step in many plants to remove toxic and other organic materials (67–69) for safety and palatability. An efficient and economical use of activated carbon for treating chemical-contaminated drinking water has been described (70).

10.2. Industrial and Municipal Wastewater Treatment. Wastewater treatment consumes about 22% of the total U.S. liquid-phase activated carbon (33), and governmental regulations are expected to increase demand over the next several years. Wastewater may contain suspended solids, hazardous microorganisms, and toxic organic and inorganic contaminants that must be removed or destroyed before discharge to the environment. In tertiary treatment systems, powdered, granular, or shaped carbon can be used to remove residual toxic and other organic compounds after the primary filtration and secondary biological treatment (71). Powdered carbon is also used in the PACT process by direct addition of the carbon to the secondary biological treatment step (53) (see WATER, INDUSTRIAL WATER TREATMENT; WATER, MUNICIPAL WATER TREATMENT).

10.3. Sweetener Decolorization. About 11% of the liquid-phase activated carbon is used for purification of sugar (qv) and corn syrup (33). White sucrose sugar is made from raw juice squeezed from sugar cane or sugar beets. The clarified liquor is decolorized using activated carbon, or ion-exchange resins (72). High fructose corn sweeteners (HFCS) are produced by hydrolysis of corn starch and are then treated with activated carbon to remove undesirable taste and odor compounds and to improve storage life. The demand for HFCS rose sharply in the 1980s primarily because of the switch by soft drink producers away from sucrose (73).

10.4. Groundwater Remediation. Concern over contaminated groundwater sources increased in the 1980s, and in 1984 an Office of Groundwater Protection was created by the EPA (33). Groundwater remediation accounts for 9% of total liquid-phase usage (33). There are two ways to apply carbon in groundwater cleanup. One is the conventional method of applying powdered, granular, or shaped carbon to adsorb contaminants directly from the water. The other method utilizes air stripping to transfer the volatile compounds from water to air. The compounds are then recovered by passing the contaminated air through a bed of carbon (74,75).

10.5. Food, Beverage, and Cooking Oil. Approximately 5% of the liquid-phase activated carbon is used in food, beverage, and cooking oil production (33). Before being incorporated into edible products, vegetable oils and animal fats are refined to remove particulates, inorganics, and organi cont aminants. Activated carbon is one of several agents used in food purification processes. In the production of alcoholic beverages, activated carbon removes haze-causing compounds from beer, taste and odor from vodka, and fusel oil from whiskey (72). The feed water for soft drink production is often treated with carbon to capture undesirable taste and odor compounds and to remove free chlorine remaining from disinfection treatment. Caffeine is removed from coffee beans by extraction with organic solvents, water, or supercritical carbon dioxide prior to roasting. Activated carbon is used to remove the caffeine from the recovered solvents (73).

10.6. Pharmaceuticals. Pharmaceuticals account for 3% of the liquid-phase activated carbon consumption (33). Many antibiotics, vitamins, and steroids are isolated from fermentation broths by adsorption onto carbon followed by solvent extraction and distillation (72). Other uses in pharmaceutical production include process water purification and removal of impurities from intravenous solutions prior to packaging (73).

10.7. Mining. The mining industry accounts for only 4% of liquid-phase activated carbon use, but this figure may grow as low-grade ores become more common (33). Gold, for example, is recovered on activated carbon as a cyanide complex in the carbon-in-pulp extraction process (72). Activated carbon serves as a catalyst in the detoxification of cyanides contained in wastewater from cyanide stripping operations (64). Problems caused by excess flotation agent concentrations in flotation baths are commonly cured by adding powdered activated carbon (72).

10.8. Miscellaneous Uses. Activated carbon removes impurities to achieve high quality. For example, organic contaminants are removed from solution in the production of alum, soda ash, and potassium hydroxide (72). Other applications include the manufacture of dyestuffs, glycols, amines, organic acids, urea, hydrochloric acid, and phosphoric acid (73). Miscellaneous uses including chemical processing account for 9% of usage (33). Several relatively low volume activated carbon uses comprise the remaining 9% of liquid-phase carbon consumption (33). Small carbon filters are used in households for purification of tap water. Oils, dyes, and other organics are adsorbed on activated carbon in dry cleaning recovery and recycling systems. Electroplating solutions are treated with carbon to remove organics that can produce imperfections when the thin metal layer is deposited on the substrate (72). Medical applications include removal of toxins from the blood of patients with artificial kidneys (73) and oral ingestion into the stomach to recover poisons or toxic materials (72,76). Activated carbon also is used as a support for metal catalysts in low volume production of high value specialty products such as pharmaceuticals, fragrance chemicals, and pesticides (77).

11. Gas-Phase Applications

Gas-phase applications of activated carbon include separation, gas storage, and catalysis. Although only 20% of activated carbon production is used for gas-phase applications, these products are generally more expensive than liquid-phase carbons and account for about 40% of the total dollar value of shipments. Most of the activated carbon used in gas-phase applications is granular or shaped. Gas phase applications account for 18% of total activated carbon. They include air purification, 42%; automotive emission control, 21%; solvent vapor recovery, 14%; cigarette filters medium, 2%; miscellaneous, 21% (33). Separation processes comprise the main gas-phase applications of activated carbon. These usually exploit the differences in the adsorptive behavior of gases and vapors on activated carbon on the basis of molecular weight and size. For example, organic molecules with a molecular weight greater than about 40 are readily removed from air by activated carbon (see ADSORPTION, GAS SEPARATION).

11.1. Solvent Recovery. Most of the activated carbon used in gas-phase applications is employed to prevent the release of volatile organic compounds into the atmosphere. Much of this use has been in response to environmental regulations, but recovery and recycling of solvents from a range of industrial processes such as printing, coating, and extrusion of fibers also provides substantial economic benefits.

The structure of activated carbons used for solvent recovery has been predominantly microporous. Micropores provide the strong adsorption forces needed to capture small vapor molecules such as acetone at low concentrations in process air (78). In recent years, however, more mesoporous carbons, specifically made for solvent recovery, have become available and are giving good service, especially for the adsorption of heavier vapors such as cumene- and cyclohexanone that are difficult to remove from micropores during regeneration (78). Regeneration of the carbon is performed on a cyclic basis by purging it with steam or heated nitrogen.

11.2. Gasoline Emission Control. A principal application of activated carbon is in the capture of gasoline vapors that escape from vents in automotive fuel systems (79). Under EPA regulations, all U.S. motor vehicles produced since the early 1970s have been equipped with evaporative emission control systems. Most other auto producing countries now have similar controls. Fuel vapors vented when the fuel tank or carburetor are heated are captured in a canister containing 0.5 to 2 L of activated carbon. Regeneration of the carbon is then accomplished by using intake manifold vacuum to draw air through the canister. The air carries desorbed vapor into the engine where it is burned during normal operation. Activated carbon systems have also been proposed for capturing vapors emitted during vehicle refueling, and activated carbon is used at many gasoline terminals to capture vapor displaced when tank trucks are filled (80). Typically, the adsorption vessels contain around 15 m^3 of activated carbon and are regenerated by application of a vacuum. The vapor that is pumped off is recovered in an absorber by contact with liquid gasoline. Similar equipment is used in the transfer of fuel from barges (81). The type of carbon pore structure required for these applications is substantially different from that used in solvent recovery. Because the regeneration conditions are very mild, only the weaker adsorption forces can be overcome, and therefore the most effective pores are in the mesopore size range (82). A large adsorption capacity in these pores is possible because vapor concentrations are high, typically 10–60%.

11.3. Adsorption of Radionuclides. Other applications that depend on physical adsorption include the control of krypton and xenon radionuclides from nuclear power plants (83). The gases are not captured entirely, but their passage is delayed long enough to allow radioactive decay of the short-lived species. Highly microporous coconut-based activated carbon is used for this service.

11.4. Control by Chemical Reaction. Pick-up of gases to prevent emissions can also depend on the chemical properties of activated carbon or of impregnants. Emergency protection against radioiodine emissions from nuclear power reactors is provided by isotope exchange over activated carbon impregnated with potassium iodide (84). Oxidation reactions catalyzed by the carbon surface are the basis for several emission control strategies. Sulfur dioxide can be removed from industrial off-gases and power plant flue gas because it is oxidized to sulfur trioxide, which reacts with water to form nonvolatile sulfuric acid (85,86). Hydrogen sulfide can be removed from such sources as Claus plant tail gas because it is converted to sulfur in the presence of oxygen (87). Nitric oxide can be removed from flue gas because it is oxidized to nitrogen dioxide. Ammonia is added and reacts catalytically on the carbon surface with the nitrogen dioxide to form nitrogen (88).

11.5. Protection Against Atmospheric Contaminants. Activated carbon is widely used to filter breathing air to protect against a variety of toxic or noxious vapors, including war gases, industrial chemicals, solvents, and odorous compounds. Activated carbons for this purpose are highly microporous and thus maximize the adsorption forces that hold adsorbate molecules on the surface. Although activated carbon can give protection against most organic gases, it is especially effective against high molecular weight vapors, including chemical warfare agents such as mustard gas or the nerve agents that are toxic at parts per million concentrations. The activated carbon is employed in individual canisters or pads, as in gas masks, or in large filters in forced air ventilation systems. In airconditioning systems, adsorption on activated carbon can be used to control the buildup of odors or toxic gases like radon in recirculated air (89).

Inorganic vapors are usually not strongly adsorbed on activated carbon by physical forces, but protection against many toxic agents is achieved by using activated carbon impregnated with specific reactants or decomposition catalysts. For example, a combination of chromium and copper impregnants is used against hydrogen cyanide, cyanogen, and cyanogen chloride, whereas silver assists in the removal of arsine. All of these are potential chemical warfare agents; the Whetlerite carbon, which was developed in the early 1940s and is still used in military protective filters, contains these impregnants (90). Recent work has shown that chromium, which loses effectiveness with age and is itself toxic, can be replaced with a combination of molybdenum and triethylenediamine (91). Oxides of iron and zinc on activated carbon have been used in cigarette filters to absorb hydrogen cyanide and hydrogen sulfide (92). Mercury vapor in air can be removed by activated carbon impregnated with sulfur (93). Activated carbon impregnated with sodium or potassium hydroxide has long been used to control odors of hydrogen sulfide and organic mercaptans in sewage treatment plants (94). Alkali-impregnated carbon is also effective against sulfur dioxide, hydrogen sulfide, and chlorine at low concentrations. Such impregnated carbon is used extensively to protect sensitive electronic equipment against corrosion by these gases in industrial environments (95). An activated carbon air filter for use in room air cleaners comprising a carbon-coated corrugated paper with a long life and high efficiency has been described (96).

11.6. Process Stream Separations. Differences in adsorptivity between gases provides a means for separating components in industrial process gas streams. Activated carbon in fixed beds has been used to separate aromatic compounds from lighter vapors in petroleum refining process streams (97) and to recover gasoline components from natural and manufactured gas (98,99).

Molecular sieve activated carbons are specially made with restricted openings leading to micropores. These adsorbents are finding increasing use in separations utilizing pressure swing adsorption, in which adsorption is enhanced by operation at high pressure and desorption occurs upon depressurization (100). Larger molecules are restricted from entrance into the pores of these carbons and, therefore, are not retained as strongly as smaller molecules. The target product can be either the adsorbed or unadsorbed gases. Examples include separation of oxygen from air and recovery of methane from inorganic gases in biogas production. Hydrogen can be removed from gases produced in the catalytic cracking of gasoline, and carbon monoxide can be separated from fuel gases. Use of pressure swing techniques for gas separation is an area of growing interest in engineering research.

The Hypersorption process developed in the late 1940s used a bed of activated carbon moving countercurrent to gas flow to separate light hydrocarbons from each other and from hydrogen in refinery operations. The application is of interest because of its scale, treating up to 20,000 m^3/h of gas, but the plants were shut down within a few years, probably because of problems related to attrition of the rapidly circulating activated carbon (101). It should be noted, however, that in recent years moving-bed and fluid-bed adsorption equipment using activated carbon has been successfully employed for solvent recovery (102).

11.7. Gas Storage. Adsorption forces acting on gas molecules held in micropores significantly densify the adsorbed material. As a result, activated carbon has long been considered a medium for lowering the pressure required to store weakly adsorbed compressed gases (103). Recent work with modern high capacity carbons has been directed toward fueling passenger cars with natural gas, but storage volume targets have not yet been attained (104). Natural gas storage on activated carbon is now used commercially in portable welding cylinders (105). These can be refilled easily at about 2000 kPa and hold as much gas as a conventional cylinder pressurized to 6000 kPa (59 atm).

11.8. Catalysis. Catalytic properties of the activated carbon surface are useful in both inorganic and organic synthesis. For example, the fumigant sulfuryl fluoride is made by reaction of sulfur dioxide with hydrogen fluoride and fluorine over activated carbon (106). Activated carbon also catalyzes the addition of halogens across a carbon–carbon double bond in the production of a variety of organic halides (77) and is used in the production of phosgene from carbon monoxide and chlorine (107,108).

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