

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Activated carbon⁽⁸⁾

A powdered, granular, or pelleted form of amorphous carbon characterized by very large surface area per unit volume because of an enormous number of fine pores. Activated carbon is capable of collecting gases, liquids, or dissolved substances on the surface of its pores. For many gases and liquids, the weight of adsorbed material approaches the weight of the carbon.

Adsorption on activated carbon is selective, favoring nonpolar over polar substances and in a homologous series, generally improving with increasing boiling point. Adsorption is also improved with increased pressure and reduced temperature. Reversal of the physical adsorptive conditions (temperature, pressure, or concentration) more or less completely regenerates the carbon's activity, and frequently allows recovery of both the carrier fluid and adsorbate. Compared with other commercial adsorbents, activated carbon has a broad spectrum of adsorptive activity, excellent physical and chemical stability, and ease of production from readily available, frequently waste materials.

Large-pore decolorizing carbons are used in liquid phase work. Applications include improving the color of manufactured chemicals, oils, and fats, as well as controlling odor, taste, and color in potable water supplies, beverages, and some foods. Gas-adsorbent carbons are generally harder, higher-density, finer pore types useful in gas separations, recovering solvent vapors, air conditioning, gas masks, and supporting metal salt catalysts, particularly in the production of vinyl-resin monomers. Uses of activated carbon are shown in Figure 2.1⁽⁹⁾.

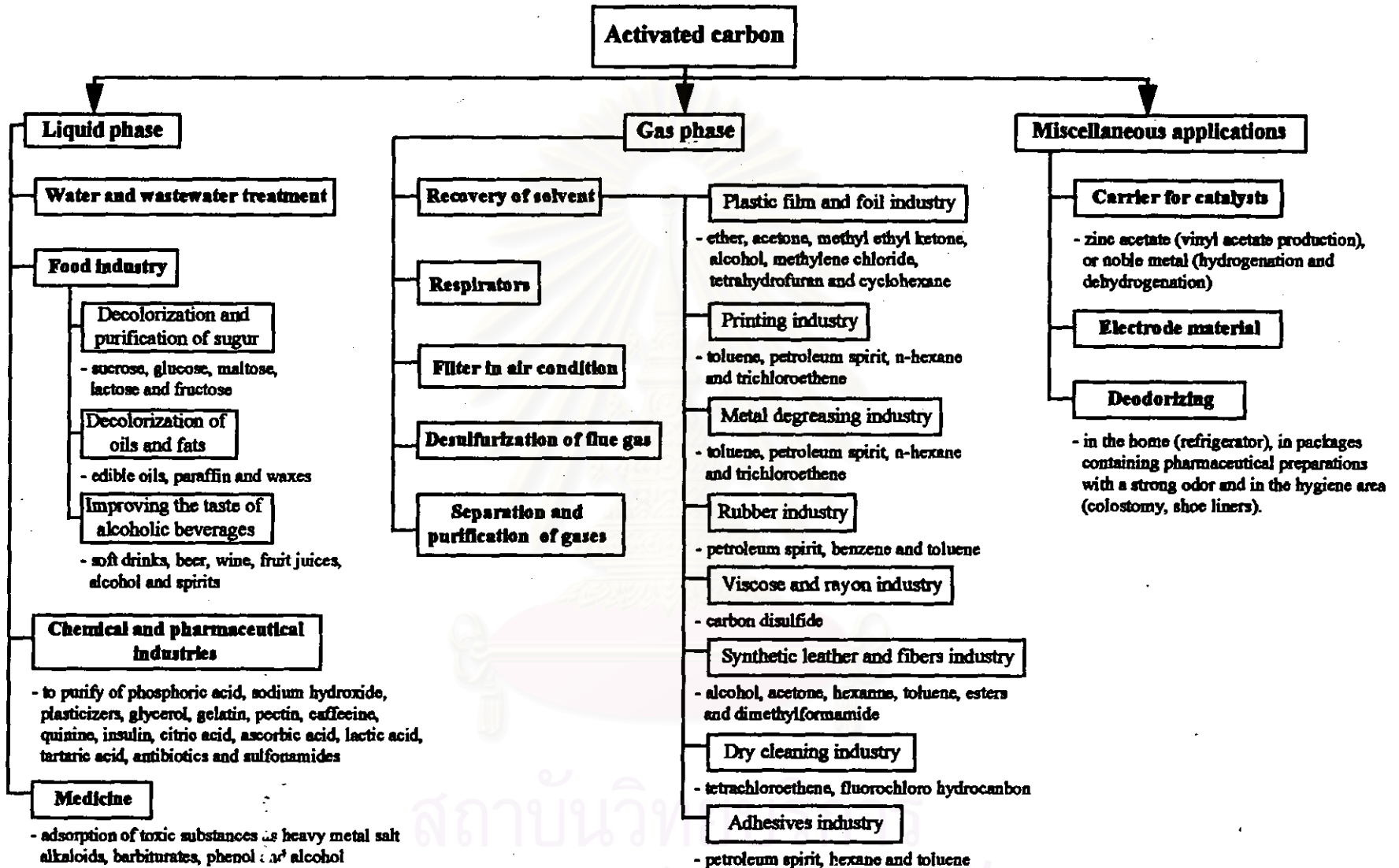


Figure 2.1 Uses of activated carbon⁽⁹⁾.

Almost any carbonaceous raw material can be used for the manufacture of activated carbon. Wood, peat, and lignite are commonly used for the decolorizing materials. Bone char made by calcining bones is used in large quantity for sugar refining. Nut shells (particularly coconut), coal, petroleum coke, and other residues in either granular, briqueted, or pelleted form are used for adsorbent products. Source materials that have been studied for the production of activated carbon^(10,11):

Bagasse	Corncobs and corn stalks	Leather waste	Petroleum acid sludge
Beet-sugar sludge		Lampblack	Potassium ferricyanide residue
Blood	Cotton seed hulls	Lignin	
Bones	Distillery waste	Lignite	Petroleum coke
Carbohydrates	Fish	Molasses	Pulp-mill waste
Cereals	Flue dust	Nut shells	Rice hulls
Coal	Fruit pits	Oil shale	Rubber waste
Coconut shells	Graphite	Peat	Sawdust
Coffee beans	Kelp and Seaweed	Polymer scrap	Wood

2.2 Structure of activated carbon

2.2.1 Elementary microcrystalline structure⁽¹²⁾

The basic structure unit of activated carbon are similar to the structure of graphite. Graphite is perhaps the simplest layered structure. The intralayer C-C distance (0.142 nm) is twice the covalent radius of aromatic carbon and the interlayer C-C distance is 0.335 nm, twice the van der Waals radius of carbon. The sheets are held together by weak van der Waals forces. Each carbon atom is three-coordinates in a planar sheet, and the fourth electron delocalized π bonds may move over the sheet. The atomic structural model of graphite is shown in Figure 2.2.

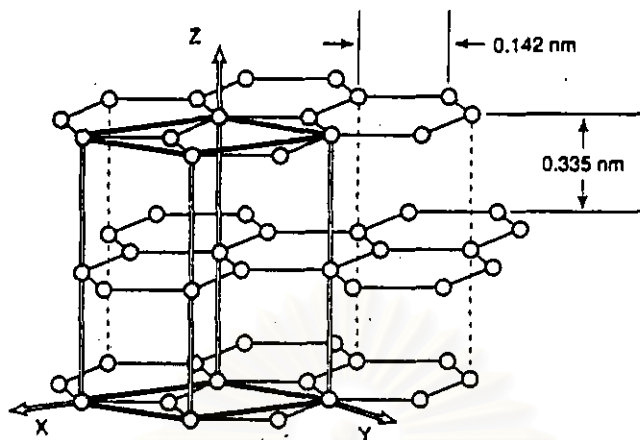


Figure 2.2 The atomic structural model of graphite⁽¹³⁾.

The structure of activated carbon is less perfectly ordered than that of graphite. On the basis of X-ray analyses Riley⁽¹²⁾ proposed two types of structure for activated carbons. The first type of structure consists of elementary crystallites; these are in two dimensions analogous to graphite, as they are composed of parallel layers of hexagonally ordered carbon atoms. The structure differs from graphite, however, in that the parallel planes are not perfectly oriented with respect to their common perpendicular axis, the angular displacement of one layer with respect to another is random and the layers overlap one another irregularly. For this arrangement Biscoe and Warren had proposed the term "*turbostratic structure*" (Figure 2.3). The mutual orientation of the elementary crystallites is completely random; their dimensions depend primarily on the temperature of carbonization. The following values are most frequently given: height, from 0.90 to 0.12 nm; width (or diameter, if a circular cross section is assumed), from about 0.20 to 0.23 nm. From this it follows that the elementary crystallites are composed of about three parallel plane graphite layers, the diameter of which is about 9 times the width of one carbon hexagon.

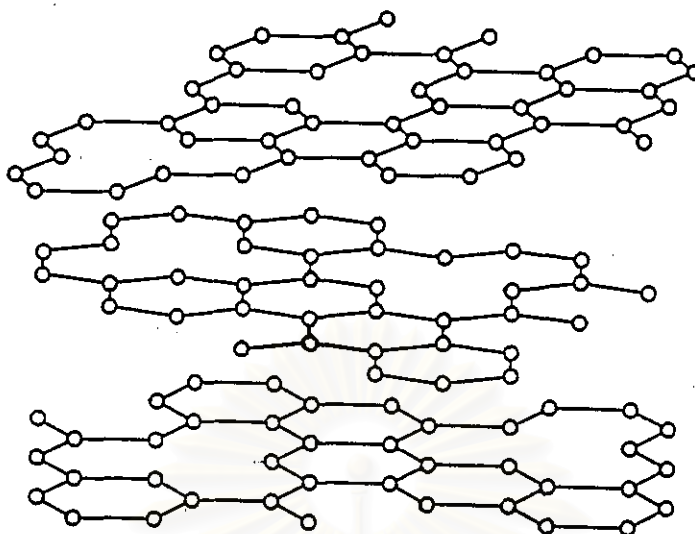


Figure 2.3 The three-dimensional crystal lattice of the turbostratic structure⁽¹³⁾.

The second type of structure, Riley describes as a disordered, cross-linked space lattice of the carbon hexagons, which results from their deflection from the planes of graphitic layers. This structure is probably stabilized by hetero-atoms, in the first place by oxygen, as it has been found in chars prepared from materials of a high oxygen content.

2.2.2 Porosity⁽¹²⁾

During the process of activation the spaces between the elementary crystallites become cleared of various carbonaceous compounds and non-organized carbon, and carbon is also removed partially from the graphitic layers of the elementary crystallites. The resulting voids are termed pores. A suitable activation process causes an enormous number of pores to be formed so that the total surface area of their walls, i.e. the internal surface of the activated carbon is very large and this is the main reason for its large adsorptive capacity. Activated carbon usually has pores belonging to several groups, each group having a certain range of values of the effective radius. Formerly pore used to be divided into three groups: micropores, mesopores, and macropores⁽¹⁴⁾.

Micropores have small sizes comparable with those of adsorbed molecules. Their effective radii are usually smaller than 1.5-1.6 nm and for average activated carbons their volumes usually lie between 0.2-0.6 cm³/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the non-porous surface, which causes a particularly large increase of adsorption capacity for small equilibrium pressures of adsorbate. In micropores, adsorption proceeds via the mechanism of volume filling. For some activated carbon, the microporous structure may have a complex nature, e.g. two overlapping microporous structure : firstly one for effective pore radii smaller than 0.6-0.7 nm and termed specific micropores, and the secondly one exhibiting pore radii from 0.6-0.7 to 1.5-1.6 nm termed supermicropores.

Mesopores, also known as transitional pores, have effective radii falling in the range of 1.5-1.6 nm to 100-200 nm. The process of filling their volume with adsorbate takes place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.1-0.5 cm³/g and their specific surface area in the range of 20-100 m²/g. The maximum of the distribution curve of their volume versus their radii is mostly in the range of 4-20 nm. Mesopores, besides their significant contribution to adsorption, also perform as the main transport arteries for the adsorbate.

Macropores are those having effective radii \geq 100-200 nm and their volume is not entirely filled with adsorbate via the mechanism of capillary condensation (it may occur only for a relative pressure of adsorbate of nearly one). The volumes of macropores are usually in the range 0.2-0.8 cm³/g and the maxima of volume distribution curves according to the radii are usually in the range 500-2000 nm. The values of their specific surface area not exceeding 0.5 m²/g are negligibly small when compared with the surface of the remaining types of pore. Consequently macropores are not of great importance in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains accessible to the particles of adsorbate.

2.3 Production of activated carbon

Activated carbon with a large adsorption capacity, it can be produced by activating the carbonized material under such conditions that the activating agent (steam, carbon dioxide, etc.) reacts with the carbon. Activation then takes place in two stages. Activated carbon can also be prepared by another procedure; in this the carbonaceous material is carbonized after the addition of substances which restricts the formation of tar (for example, zinc chloride). In this way a carbonized product with the properties of very good activated carbon can be obtained in a single operation. Thus, activated carbon can be produced in one of two ways⁽¹²⁾:

- By carbonizing material with the addition of activating agents ($ZnCl_2$, $CaCl_2$, H_3PO_4) which influences the course of pyrolysis. This method is generally known as "chemical activation".

- By allowing the inactive carbonized product (prepared by the usual methods of carbonization) to react with usually suitable gaseous substances (steam, carbon dioxide, oxygen). This method is generally known as "physical activation".

2.3.1 Chemical activation

In a chemical activation⁽¹⁵⁾ process the lignocellulosic precursor is mixed with a chemical restricting the formation of tars and, the amount of the aqueous phase in the distillate (acetic acid, methanol, and other) is also less than in normal carbonization and, after kneading, carbonized and washed to produce the final activated carbon. The most widely used activation agents⁽⁹⁾ are

Aluminum chloride	Chlorine	Phosphorus pentoxide	Sodium hydroxide
Ammonium chloride	Hydrogen chloride	Potassium metal	Sodium hydroxide
Borates	Iron salt	Potassium hydroxide	Sodium oxide
Boric acid	Nickel salt	Potassium permanganate	Sulfur dioxide
Calcium chloride	Nitric acid	Potassium sulfide	Sulfuric acid
Calcium hydroxide	Nitrous gases	Phosphoric acid	Zinc chloride

The chemical incorporated to the interior of the precursor particle reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinkage of the particle. In this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a high degree of porosity results. Chemical activation offers several advantages⁽¹⁵⁾, as (i) it is performed in one stage, combining carbonization/activation, (ii) it yields higher carbon products, (iii) it needs lower temperatures, and (iv) in most cases part of the added chemicals are easily recovered. However, chemical activation involves hazardous chemicals and the recovery of these chemicals from the products or off gases results in multiple operations. Nonrecovery of the chemicals not only renders the process uneconomical but contributes to environmental pollution.

Chemical activation⁽¹²⁾ is usually carried out at temperatures from 400-600°C. The variables with direct incidence in the development of porosity are the degree (coefficient) of impregnation; this is the weight ratio of the anhydrous activation salt to the dry, starting material and the temperature of heat treatment. The chemical is introduced into the precursor, where it produces physical and chemical changes, modifying the thermal degradation process. As a consequence, the temperature of the process does not need to be high. During impregnation and especially during evaporation, there is a weakening of the precursor structure, a hydrolysis reaction (with loss of volatile matter), an increase in elasticity, and swelling of the particle. The effect of the degree of impregnation on the porosity of product is apparent from the fact that the volume of salt in the carbonized material equals the volume of pores which are freed by its extraction. For small degree of impregnation, the increase in the total pore volume of the product with increase in the degree of impregnation is due to the increase in the number of small pores. When the degree of impregnation is further raised, the number of larger-diameter pores increases and the volume of the smallest decreases. Upon carbonization, the formation of tar is restricted with the formation of solid carbon, and this prevents somewhat the contraction of the particle. After carbonization, most of the chemical is still in the particle, and the intense washing to eliminate it produces the porosity. This means that the amount and distribution of the

chemical incorporated in the precursor govern the porosity of the carbon, thus making this activation very flexible for the production of activated carbon with different pore size distributions.

2.2.2 Physical activation

2.3.2.1 Carbonization⁽¹⁴⁾

Carbonization is one of the most important steps in the production process of activated carbons since it is in this course which the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them and apparently as the result of deposition and decomposition of tarry substances, these become filled or at least blocked by disorganized ("amorphous") carbon. The chars from carbonization ought to be characterized: (i) uniformly black (ii) shiny surface (iii) sharp and (iv) low ash content. The carbonized product has only a very small adsorption capacity. Presumably, at least for carbonization at lower temperatures (400–600°C), part of the tar remains in the pores between the crystallites and on their surface. A carbon with a large adsorption capacity, however, can be produced only by activating the carbonized material under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon.

Carbonizates of requisite properties⁽¹⁴⁾ are obtained by suitable adjustment of the conditions of pyrolysis of the carbonaceous material. These relevant parameters are: (i) the final temperature achieved, (ii) the time of carbonization, (iii) the rate of temperature increase, and (iv) the atmosphere in which the pyrolysis is conducted.

The most important of these parameters is the final temperature of the process ; this is associated with the need to supply to the macromolecules of coal significant amounts of energy in order to produce splitting of the weaker chemical bonds and to enable migration of the volatile products of thermal decomposition of the raw material to the granule or grain environment. The carbonization temperature is increased, the condensation processes in the material are enhanced and the greater becomes the mechanical strength of the resulting granules. The condensation of the material associated with the decrease of its pore volume results in a decrease of reactivity of the granules in the succeeding activation process (Table 2.1). The volume of the micropores is in this case so small as to be inaccessible to benzene molecules.

Table 2.1 Effect of the final temperature of carbonization on the properties of granules⁽¹⁴⁾.

Final carbonization temperature (°C)	Mechanical strength of the granules (%)	Bulk density of granules (g/cm ³)	Rate of oxidation with CO ₂ at 870°C (g(g/min) ⁻¹)	Activation energy of the granules (kJ/mol)
400	unstable	0.62	-	-
500	72.7	0.60	-	-
600	93.8	0.61	0.00194	212
700	98.0	0.65	0.00156	237
800	98.4	0.69	0.00134	256

The residence time of the carbonaceous material at the final carbonization temperature has an effect on the ordering of the compact structure of the carbon material. We distinguish here two principal temperatures at which the effect of time is different:

(i) A temperature lower than that at which the main thermal decomposition reactions appropriate to the given raw material are terminated.

(ii) A temperature higher than that of the internal transformations at which the final porous structure of the carbonizate is established.

In the first case, further slow thermal decomposition of the carbon material continues over time. However, some part of the decomposition processes has become inhibited. The carbonizate obtained under these conditions shows a greater reactivity towards the activating agents than that in which the reactions of the volatile pyrolysis products between each other and the carbon material, the ordering of the chemical structure of the carbon material, and the generation of carbon crystallites have been brought to an end.

In the second case, i.e. at a temperature higher than that at which the main thermal decomposition processes are terminated, with elapse of time a further ordering of the internal structure of the carbon material proceeds with the possible generation of crystallites. As carbonization continues, the volume of the smallest pores usually decreases due to the further decrease of the volume of the carbonized mass. For the reasons described, the longer obtained carbonizate is maintained at the final carbonization temperature, the lower its reactivity.

Table 2.2 Effect of the rate of heating on the properties of carbonized granules⁽¹⁴⁾.

Heating rate (°C/min)	Mechanical strength of the granules (%)	Bulk density of granules (g/cm ³)	Pore volume of granules (cm ³ /g)			
			total	micropores	mesopores	macropores
1	93.0	0.71	0.24	-	-	-
5	94.0	0.70	0.22	0.12	0.01	0.09
8	94.1	0.72	0.23	-	-	-
20	91.5	0.62	0.28	-	-	-
stepwise growth	60.0	0.28	1.09	0.11	0.03	0.96

An important parameter of the carbonization process is the rate at which the final temperature is achieved. When the temperature is raised rapidly, the particular phases of the thermal decomposition of coal and the secondary reactions of the pyrolysis products with each other overlap, so control of the establishment of the porous structure in the carbonizate is more difficult. Neither does a high rate of increase of temperature favor higher ordering of the chemical structure of the carbon material, since the processes taking place in the solid phase proceed fairly slowly and therefore require time. If the temperature is raised rapidly, a large quantity of volatile matter evolves within a short time, and as a result pores of greater sizes are usually formed. The reactivity of the carbonizates obtained in this way is greater than that of the products heated at a slow rate. This is due to the greater porosity and reduced ordering of the compact carbon material as compared with carbonizates obtained from the same raw material but at a low rate of heating.

The thermal decomposition of carbonaceous material and the course of the secondary mutual reactions of the pyrolysis products and the reactions of the latter with the solid carbonizate are also affected by the atmosphere in which the carbonization process is conducted. If the gases and vapors evolving during pyrolysis are rapidly removed by a neutral gas or combustion gases, then the quantity of the carbonizate obtained is smaller but its reactivity is greater. This is clearly evident when the combustion gases contain large amounts of a water vapor and carbon dioxide, since then they react additionally with the decomposing carbonaceous material even at relatively low temperature.

The main aim of the carbonization process is to generate in the granules and grains the required porosity and ordering of structure of the compact carbon material. This ordering should be much greater than that of the raw material used. Both these factors have a crucial effect on the reactivity of the carbonizate in its reaction with the gaseous activating agent. This reactivity increases (i) with the degree of porosity generated and (ii) with reduction in the ordering of the compact carbon matter. A large volume of pores in the carbonizate facilitates the diffusion of the gaseous

activator into the granules and ensures a large surface area on which chemical reactions may take place.

2.3.2.2 Activation⁽¹²⁾

The oxidizing agents most often used are steam, carbon dioxide, oxygen (air). During the activation of the carbonized product first the disorganized carbon is removed, and by this the surface of the carbon crystallites becomes exposed to the action of the oxidizing agent. Details of the mechanism of this process, however, are not yet reliably understood. A possible explanation is that the velocity with which the crystallites burn is larger in the direction parallel with the plane of the carbon layers than in the direction perpendicular to this plane; the crystallites orientated perpendicularly to the surface exposed to the action of the oxidizing agents can, therefore, be more easily attacked and burn out more quickly.

The removal of unorganized carbon and the non-uniform burn-out of elementary crystallites leads in the first phase of activation to the formation of new pores to the development of the macroporous structure. In the subsequent phases, however, the effect which becomes increasingly significant is the widening of existing pores, or the formation of larger size pores by the complete burn-out of walls between adjacent micropores. This leads to an increase in the volume of transitional and macropores, whereas the volume of micropores diminishes. As a measure of the degree of activation the so called burn-off is usually used, which is the percentage weight decrease of the material during activation, referred to the original carbonized product. Sometimes the so called activation yield is used, which is the weight of the resulting activated carbon expressed as a percentage of the carbonized intermediate product prior to activation. The burn-off (B) and the activation yield (A) are related thus:

$$B = 100 - A$$

According to Dubinin⁽¹⁶⁾, when the burn-off is less than 50%, a microporous activated carbon is obtained; when it is large than 75% (which occurs at high reaction times), a macroporous product is obtained; and when the burn-off is between 50 and 75%, the product is of mixed structure and contains both micro- and macropores.

The carbon atoms⁽¹²⁾ which form the structure of the carbonized product differ markedly from one another in their affinity towards the activation agent. Those at the edges and corners of elementary crystallites, and those situated at defective places of the crystal lattice, are more reactive, because their valencies are incompletely saturated by interaction with neighbouring carbon atoms. These places are the so called "active sites" on which reaction with the activation agent occurs; these sites represent only a small part, at the most only a few percent, of the total surface exposed to the reaction. In the reaction of a gaseous activation agent with carbon, complex surface compounds are temporarily formed on the active sites, and on their decomposition the oxidized carbon is removed from the surface as gaseous oxides (carbon monoxide or dioxide); as a result of this, new incompletely saturated carbon atoms become exposed on the surface of the crystallites and the active sites are thus again prepared to react with further molecules of the activation agent. Details of the mechanism by which carbon reacts with steam, carbon dioxide and oxygen are shown below:

- Activation with steam ^(12,14)

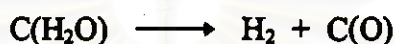
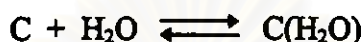
The reaction of steam with carbon is endothermic and a stoichiometric equation has the form :



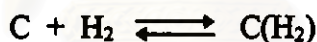
The rate of gasification of carbon by a mixture of steam and hydrogen is given by the formula:

$$v = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2O} + k_3 P_{H_2}} \quad (2.1)$$

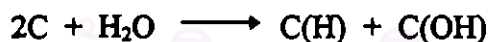
where : P_{H_2O} and P_{H_2} are the partial pressures of steam and hydrogen, respectively, k_1, k_2, k_3 are the experimentally determined rate constants. The following reaction scheme is accepted as highly probable:



The inhibiting effect of hydrogen can be ascribed to its occupying active centers on which it becomes adsorbed:



Long and Sykes⁽¹²⁾ assume that the first step of the reaction is the dissociated adsorption of water molecules according to the scheme:



Hydrogen and oxygen are adsorbed at neighbouring active sites which account for about 2 percent of the surface area.

The reaction of steam with carbon is accompanied by the secondary reaction of water-gas formation which is catalysed by the carbon surface:



Reif⁽¹²⁾ explained the presence of carbon dioxide and the catalytic surface effect of carbon surface on its formation by the reaction:



Activation with steam is carried out at temperatures from 750 to 950°C with the exclusion of oxygen which at these temperatures aggressively attacks carbon and decreases the yield by surface burn-off. It is catalysed by the oxides and carbonates of alkali metals, iron, copper and other metals; the activation catalysts usually employed in practice are carbonates of alkali metals, which are added in small amounts to the material to be activated.

- Activation with Carbon Dioxide ^(12,14)

For the rate of gasification of carbon by carbon dioxide an equation analogous to that for the reaction with steam has been derived:

$$v = \frac{k_1 P_{\text{CO}_2}}{1 + k_2 P_{\text{CO}} + k_3 P_{\text{CO}_2}} \quad (2.2)$$

where: P_{CO_2} and P_{CO} are the partial pressures, and k_1, k_2, k_3 are the experimentally determined rate constants. Although the quantitative validity of this equation has been subject to criticism, it is taken as a basis for consideration of the mechanism of the reaction of carbon dioxide with carbon.

The rate of this reaction is retarded not only by carbon monoxide, but also by the presence of hydrogen in the reaction mixture. When from the possible hypothetical schemes which satisfy Equation (2.2) those are eliminated which include stages that

have been experimentally shown to be improbable, two basic variants of the reaction mechanism remain:



The basic difference between the two schemes lies in the explanation of the inhibiting effect of carbon monoxide. The rate of the reaction depends on the number of free active sites; in variant A the rate of the reverse reaction (2.3) is considered to be negligible and the inhibiting effect of carbon monoxide is supposed to be due to the blocking of active sites by their being covered by the adsorbed carbon monoxide [Equation (2.5)]. According to variant B the rate of the reverse reaction (2.3) is considered to be significant, and the effect of carbon monoxide is explained as being due to a displacement of the reaction equilibrium in accordance with Equation (2.6). Reaction (2.4) is considered by the majority of authors to be very slow.

Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature 850-1100°C. The activation agent used in technical practice is flue gas to which a certain amount of steam is usually added, so that actually this is a case of combined activation. The catalyst for the reaction with carbon dioxide are carbonates of alkali metals.

- Activation with Oxygen (air) ^(12,14)

In the reaction of oxygen and carbon both carbon monoxide and carbon dioxide are formed according to the equations :



Both reactions are exothermic. The mechanism of the reaction of carbon with oxygen is not yet fully understood; the most discussed point was whether carbon dioxide is a primary product of carbon oxidation or the monoxide is formed first and the dioxide is the product of secondary reaction. According to the present state of knowledge it may be assumed that both oxides are primary products. The value of the ratio CO/CO₂ increases with the increase of temperature.

The reactions with oxygen being exothermic, it is not easy to maintain the correct temperature conditions in the oven; it is especially difficult to avoid local overheating which prevents the product from being uniformly activated. Furthermore, because of the very aggressive action of oxygen, burn-out is not limited to the pores but also occurs on the surface of the grains, causing great loss. Carbons activated with oxygen have a large amount of surface oxides.

2.5 Estimation of the properties of activated carbon

The commercial use of activated carbons, their transport, storage and sales require knowledge of the properties of these materials⁽¹⁴⁾. The methods for estimating these properties are approved by the members of the Activated Carbons Sector Group of the European Council of Chemical Manufacturers' Federations (CEFIC). The tests require highly professional laboratories and advanced equipment. Most of the testing methods have been developed and approved by such organizations as the American

Society for Testing Materials (ASTM), the American Water Works Association (AWWA), the Deutsches Institut für Normung e.V. (DIN), or the International Organization for Standardization (ISO). In this work ASTM was used for estimating the properties of the resulted activated carbon.

2.5.1 B.E.T. Surface area ⁽¹⁷⁾

To measure total surface area, nonspecific physical adsorption is required, but even with physical adsorption the isotherm varies somewhat with the nature of the adsorbent (the solid). Most physical adsorption isotherms may be grouped in to five types, as originally proposed by Brunauer, Deming, Deming, and Teller (BDDT). More recently, the grouping has generally been termed the *Brunauer, Emmett, and Teller (BET) classification*. In all cases the amount of vapor adsorbed increases as its partial pressure is increased, becoming at some point equivalent to a monolayer, but then increasing to a multilayer, which eventually merges into a condensed phase as the relative pressure, P/P_0 approaches unity.

Type I is frequently called the Langmuir type. The asymptotic value was originally ascribed to a monolayer, as derived from the Langmuir equation. However, this isotherm is seldom encountered on nonporous materials. The isotherm shape is fairly commonly observed with microporous substances having relatively small external surfaces, such as certain activated carbons and zeolites. In these cases the volume of the pores is so much greater than the volume corresponding to a monolayer or multilayer or a multilayer a few molecules thick that what appears to be an asymptotic value occurs at a relative pressure substantially less than unity, corresponding to complete filling of micropores rather than to monolayer adsorption.

Type II, sometimes termed the *sigmoid* or *S-shaped isotherm*, is commonly encountered of nonporous structures of macroporous materials. Point *B* occurs at a

“knee” (Figure 2.4) and is the stage at which monolayer coverage is complete and multilayer adsorption begins.

Type III isotherm is convex over the entire range and does not exhibit a point *B*. It is relatively rare and is typical of a system in which the forces of adsorption are relatively weak, as when the adsorbate is not wetted by the surface, e.g., water vapor on graphite.

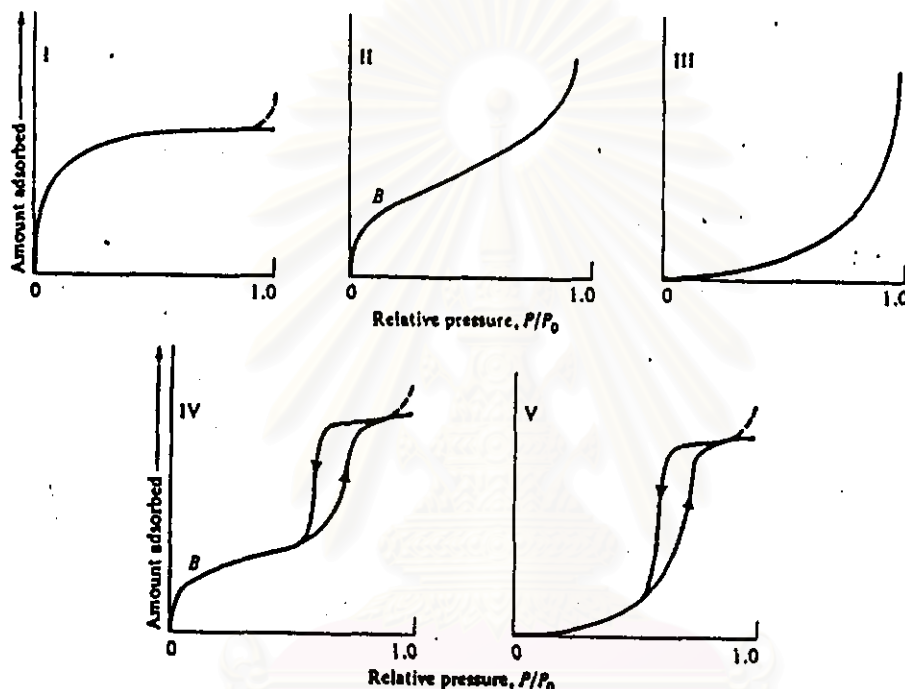


Figure 2.4 The main types of isotherms of adsorption of gases and vapors⁽¹⁴⁾.

Type IV is encountered with materials having pores in the general range of 2 to 50 nm (mesopores). At low values of P/P_0 the isotherm is similar to type II, but then adsorption increases markedly at higher values of P/P_0 where pore (capillary) condensation takes place. A hysteresis effect associated with this pore condensation is usually observed. Isotherms of this type are often encountered with industrial catalysts, and the capillary condensation curve may be used to determine a pore-size distribution.

Type V is similar to *type III*, but with pore condensation taking place at higher values of P/P_0 . It also relatively rare.

The most common method of measuring surface area, and one used routinely in most catalyst studies, is that developed by Brunauer, Emmett, and Teller. Early descriptions and evaluations are given by Emmett. In essence, the Langmuir adsorption isotherm is extended to multilayer adsorption. As in the Langmuir approach, for the first layer the rate of evaporation is considered to be equal to the rate of condensation, and the heat of adsorption is taken to be independent of coverage. For layers beyond the first, the rate of adsorption is taken to be proportional to the fraction of the lowest layer still vacant. The rate of desorption is taken to be proportional to the amount present in that layer (These assumptions are made largely for mathematical convenience). The heat of adsorption for all layers except the first layer is assumed to be equal to the heat of liquefaction of the adsorbed gas. Summation over an infinite number of adsorbed layers gives the final expression as follows :

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (2.7)$$

where V = volume of gas adsorbed at pressure P
 V_m = volume of gas adsorbed in monolayer, same units as V
 P_0 = saturation pressure of adsorbate gas at the experimental temperature
 C = a constant related exponentially to the heats of adsorption and liquefaction of the gas

$$C = e^{(q_1 - q_L)RT} \quad (2.8)$$

where q_1 = heat of adsorption on the first layer
 q_L = heat of liquefaction of adsorbed gas on all other layers
 R = the gas constant

If Equation (2.7) is obeyed, a graph of $P/V(P_0-P)$ versus P/P_0 should give a straight line, the slope and intercept of which can be used to evaluate V_m and C . Many

adsorption data show very good agreement with the BET equation over values of the relative pressure P/P_0 between approximately 0.05 and 0.3, and this range is usually used for surface area measurements. At higher P/P_0 values, complexities associated with the realities of multilayer adsorption and/or pore condensation cause increasing deviation. With microporous substances such as zeolites, the linear region on a BET plot occurs at much lower values of P/P_0 , typically around 0.01 or less.

2.5.2 Physical test ⁽¹⁴⁾

- *Bulk density.* The bulk density is defined as the mass per unit volume of the activated carbon sample in air including both the pore system and the void between the particles. The bulk density of activated carbon, depending on the shapes, sizes and densities of the individual particles is indispensable for determining the size of unit packages.

2.5.3 Adsorption tests ⁽¹⁴⁾

The adsorption properties of activated carbon is generally estimated by determining the isotherms of adsorption from the liquid phase. The determination of the adsorption of one test substance from an aqueous solution is often insufficient for characterizing the adsorption properties of a carbon. Thus the properties of activated carbons are estimated by comparing the results of measurements for different adsorbates, e.g. by comparing the adsorptions of fairly large molecules of methylene blue or iodine.

- *Iodine adsorption.* The study of the process of iodine adsorption and also the determination of the iodine number is a simple and quick test for estimating the specific surface area of activated carbon. The iodine number is defined as the number of milligrams of iodine adsorbed by 1 g of activated carbon from an aqueous solution when the iodine concentration of the residual filtrate is 0.02 N. If the final values

obtained are different from 0.02 N but lie in the range of 0.007-0.03 N, appropriate corrections are necessary. In this method it is assumed that iodine at the equilibrium concentration of 0.02 N is adsorbed on the carbon in the form of a monolayer, and this is the reason why there is a relationship between the iodine number of activated carbon and its specific surface area which may be determined, for example, by the BET method. The specific surface areas of activated carbons with highly developed microporous structures as determined by the iodine number method are too low. This is because iodine is adsorbed chiefly on the surface of pores much larger than 1 nm, while in activated carbons with large specific surface areas the proportion of very fine pores inaccessible to iodine molecules is significant.

- *Methylene blue adsorption.* The methylene blue value gives an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene blue, it also gives an indication of the specific surface area of the carbon which results from the existence of pores of dimensions greater than 1.5 nm.

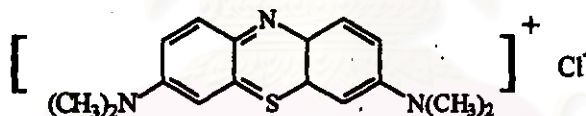


Figure 2.5 The chemical structure of methylene blue⁽¹⁴⁾.

2.5.4 Physico-chemical Test ⁽¹⁴⁾

- *Volatile matter content.* The international standard used for determination of volatile matter in hard coal and coke is also applicable to activated carbon. A sample of powdered (<0.1 mm) activated carbon is heated at 950 ± 25 °C for $7 \text{ min} \pm 10 \text{ s}$. Volatile matter content is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions.

- *Moisture content.* A simple method of determining the water content is drying activated carbon in a dryer. The sample of powdered (1-2 g) or granular (5-10 g) carbon is dried at 150°C to constant weight (usually about 3 hr). The weight loss is expressed as a percentage of the weight of the original sample.

- *Ash content.* The ash content in various types of activated carbon varies over a wide range, depending primarily on the type of raw material. The relative ash content also increases with increase in the degree of burning of the coal during activation. Ash consists mainly of oxides and, in smaller amounts, of sulfates, carbonates, and other compounds of iron, aluminum, calcium, sodium, potassium, magnesium and many other metals. Depending upon the type of raw material, it may comprise different and often fairly large quantities of silicon. The commonly used method of removing ash is to leach activated carbon with acids. Due to the complex composition of ash, mixture of acids, e.g. hydrochloric or hydrofluoric acid, are often used if ash contains substantial quantities of silicon.

The ash content of activated carbon can be determined by ignition of the crucible in an electric muffle furnace. Ignition is conducted at 650 ± 25 °C for 3 to 16 hr, depending on the type of activated carbon and dimensions of its particles, to constant mass. The weight of the ash carbon is expressed as a percentage of the weight of the original carbon sample.

2.6 Literature review

Torikai *et al.* (1979)⁽¹⁸⁾ studied the preparation of activated carbon from used tires by pyrolysis of samples at 550°C and activating the residual solid so obtained in a stream of CO₂ at 900°C. This carbon had surface area of up to 400 m²/g.

Ogasawara *et al.*(1987)⁽¹⁹⁾ prepared activated carbon from used tires by pyrolysis and activation in a one stage. Approximate 1 g of the sample was dumped in quartz tube reactor of 10 mm inside diameter. The tire sample was treated at 900°C

for 1 hr with steam at a flow rate of 0.75 mg of water/g of sample/s and helium at a flowrate of 0.67 mL/s. The carbon residue had a surface area of 1260 m²/g, but the carbon yield was only 9 wt % of the original tire material.

Marchant and Petrich (1993)⁽²⁰⁾ prepared activated carbon from used tires by pyrolysis and steam activation. Tires were pyrolysis in a straight inconel tube (1.3 cm OD and 10 cm long) heat in a fluidized sand bath at 530°C for 60 min. About 0.5 mL of water was injected into the system every 2 min (0.014 mol/min). The nitrogen flow rate was 0.59 g/min (0.021 mol/min). A maximum in surface area was 607 m²/g and micropore area was 560 m²/g.

Teng *et al.* (1995)⁽⁶⁾ studied the preparation of activated carbon from used tires by pyrolysis of samples at 900°C at a heating rate of 30°C/min, and activated in 0.16 atm CO₂ in TG reactor. Pyrolysis and activation were carried out in helium. Two tire samples were used in this investigation: granulated and nongranulated rubber. The granulated sample was prepared by crushing and grinding a large piece of frozen tire under cryogenic conditions. The sample particle size was less than 300 μm. The nongranulate sample was prepared by cutting the tire rubber to a fixed of 170 ± 5 mm. Granulated tires produced activated carbon with a surface area of 734 m²/g and nongranulated tires produced activated carbon with a surface area of 860 m²/g. In order to study the effect of oxygen pretreatment, a sample was prepared by exposing the granulated tires with air at 140°C for 15 days and following activation at 900°C with 0.16 atm CO₂; as a result, activated carbon was the highest char yield and surface area (952 m²/g).

Williams, Besler and Taylor (1996)⁽⁴⁾ pyrolysed used tires in a 200 cm³ static batch reactor in a N₂ atmosphere. The compositions and properties of the derived gases, pyrolytic oils and solid char were determined in relation to pyrolysis temperatures up to 720°C and at heating rates between 5 and 80°C/min. When pyrolysis temperature was increased, the percentage mass of solid char decreased while

gas and oil products increased until 600°C after which there was a minimal change to product yield, the used tires producing approximately 55% oil, 10% gas and 35% char. The gases were identified as H₂, CO, CO₂, C₄H₆, CH₄ and C₂H₆, with lower concentrations of other hydrocarbon gases. FT-IR analysis of the oils indicated the presence of alkanes, alkenes, ketones or aldehydes aromatic, polyaromatic and substituted aromatic groups.

Tancredi *et.al.* (1996)⁽²¹⁾ prepared activated carbon from eucalyptus wood chars. The results of CO₂, CO₂-O₂ and steam activation were compared. The sawdust of eucalyptus 0.5-1.6 mm was first carbonized in a continuous N₂ flow (100 mL/min at s.t.p.) in a horizontal tube furnace consisting of a 75 mm diameter quartz tube heated electrically. The carbonization temperature was maintained 400-800°C for 2 hr. The chars obtained from this carbonization step were sieved and the 0.5-0.8 mm size fraction was activated in the same furnace using CO₂, steam and CO₂-O₂ mixtures as activating agents. Activated carbon obtained from CO₂ activation at the 800°C had surface area of 780 up to 1190 m²/g. But activated carbon obtained from steam activation at 800°C had surface area of 810 up to 1190 m²/g. The carbonization step gave rise to a narrow micropore structure and highly developed macroporosity which increased slightly upon CO₂ activation and significantly upon steam activation. This last process led also to a widening of micropore size distribution and developed the mesoporosity more than CO₂ activation did. As steam had a higher reactivity than CO₂, diffusional limitations could be more significant and would favour gasification in large pores, giving rise to meso- and macroporosity development. This was also consistent with the increase in meso- and macropore volumes with increasing steam activation temperature. The presence of O₂ accompanying CO₂ in the activating gas small increased the micro- and macroporosity of the carbons, compared with pure CO₂ activation.

Ratikorn Isarasaene (1996)⁽²²⁾ produced activated carbon from used tires by carbonization and superheated steam activation. Carbonization was conducted in a fixed bed reactor, 150 mm diameter and 1100 mm length. This study was found that the optimum condition for 1 kg of used tires 5 x 5 x 5 mm in dimension, was at 450°C

for 30 min under nitrogen atmosphere. The char product yield was 47.20% which consisted of 50.48% fixed carbon, 23.11% volatile matter and 23.41% ash. The superheated steam activation was operated in a fixed bed reactor, 38.1 mm diameter and 200 mm length. The optimum condition for activation was 50 g of carbonized char at 900°C for 30 min with superheated steam input rate of 1.88 g/min and air input rate of 43 cm³/s. The char particle size is 1.18-2.36 mm. The activated carbon obtained iodine number of 891.11 mg/g, methylene blue number of 172.03 mg/g, bulk density of 0.44 g/cm³, and ash content of 29.05%.

Sai *et al.* (1997)⁽²³⁾ produced activated carbon from coconut shells chars using steam or carbon dioxide as the reacting gas in a 100 mm diameter and 1250 mm length fluidized bed reactor. Experimental data showed that an increase in reaction time, fluidizing velocity, particle size and temperature resulted in better activation. However, at higher reaction times, a decrease in iodine numbers was observed, which was due to coalescence or widening of already formed pores. Static bed heights greater than the diameter of the column gave lower iodine numbers due to poor gas - solid contact, because of slugging. Steam as the activating gas enhanced the activation compound to a mixture of steam and CO₂ or pure CO₂. From the experimental data, it was observed that maximum iodine number could obtained for the following process condition: fluidization velocity of 24.7 cm/s; particle size of 1.55 mm; static bed height of 100 mm; temperature of 850°C; fluidizing medium, steam and raw material, coconut shells chars.

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