CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Activated carbon

Activated carbon[9] is a processed carbon material with a highly developed porous structure and a large internal specific surface area. If you take a look at a cross section of an activated carbon particle, it looks like a beehive. It consists, principally of carbon (87 to 97%), but also contains such elements as hydrogen, oxygen, sulfur and nitrogen, as well as various compounds either originating from the raw material used in its production or generated during its manufacture.

Activated carbon has the ability to adsorb various substances both from the gas and liquid phases. It is widely used for adsorption of pollutants from gaseous and liquid steams, for recovery of solvent and as a catalyst or catalyst support. In the nuclear industry, activated carbon is used for adsorption of iodine and noble gases from gaseous effluents. One of the most important fields in terms of consumption is in water and wastewater treatment. To obtain these activated carbons from cheap and readily available precursors become an interesting objective.

2.2 Raw materials for the production of activated carbon [9,10]

The principal properties of manufactured activated carbons depend on the type and properties of the raw material used. Any cheap substance with a high carbon and low ash content can be used as a raw material for the production of activated carbon. In Europe the most important raw materials used for this purpose are wood (sawdust), charcoal, peat, peat coke, certain types of hard and brown coal, and the semi-coke of brown coal. To produce activated carbon, which should exhibit high adsorption

capacity and a large volume of the smallest pores (micropores), coconut shells are usually used. In the USA, brown carbons and petroleum products are widely used for manufacturing activated carbons. Source materials that have been studied for the production of activated carbon[10]:

Bagasse	Corncobs and corn	Leather waste	Petroleum acid sludge
Beet-sugar sludges	stalks	Lampblack	Potassium ferricyanide
Blood	Cotton seed hulls	Lignin	residue
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

2.3 Production of activated carbon

Activated carbon is usually production by the carbonization and activation of carbonaceous materials.

2.3.1 Carbonization (or pyrolysis) [9]

The carbonaceous material that constitutes the basis for the production of activated carbon by the steam-gas method must meet certain requirements among which the most important are : (i) low content of volatile matter, (ii) high content of elemental carbon, (iii) definite porosity and (iv) sufficient strength of attrition. Of course, raw materials do not meet all these requirements simultaneously and therefore they require carbonization.

This is one of the most important steps in the production process of activated carbons since it is in the course of carbonization that 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. There are three clear stages in the carbonization process: (a) loss of water in the 27-197°C range; (b) primary pyrolysis in the 197-497°C range with evolution of most gases and tars with formation of the basic structure of the char; (c) consolidation of char structure at 497-847°C with a very small weight loss. The resulting 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.

2.3.2 Activation [9,10]

Generally, there are two main types of production of activated carbon :

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

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

2.3.2.1 Chemical activation

For chemical activation[7, 10], the common chemicals used are dehydrating agent such as $ZnCl_2$, $CaCl_2$, $MgCl_2$ and some acids such as H_3PO_4 and H_2SO_4. The activation agent influences the pyrolytic processes so that the formation of tar is restricted to a minimum and the amount of the aqueous phase in the distillate is also less than that in the normal carbonization. The activation agent also changes the chemical nature of the cellulose substance by dehydration, which decomposes the organic substances by the action of heat and prevents the formation of tar.

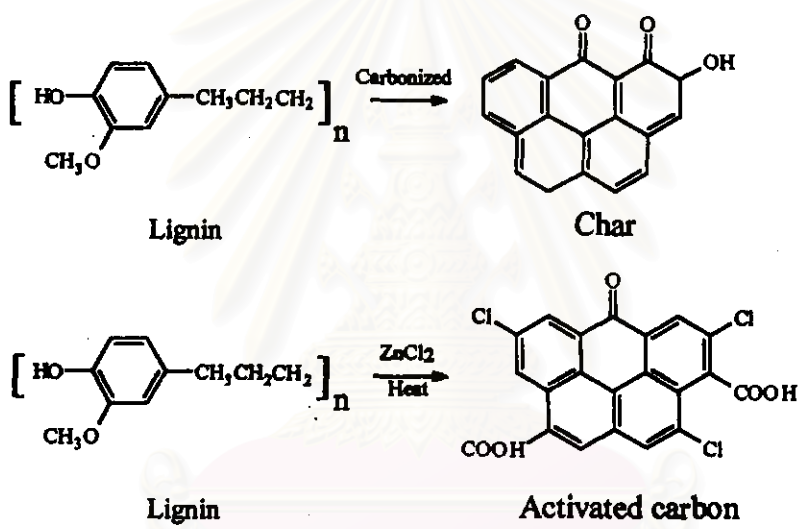

Figure 2.1 Chemical reaction of lignin with activated by $ZnCl_2$[9].

Chemical activation[7] is usually carried out at temperatures from 400-600°C. These temperatures are lower than those needed for activation with gaseous agent (physical activation). An important factor in chemical activation is the degree (coefficent) of impregnation ; this is the weight ratio of the anhydrous activation salt to the dry starting material. The effect of the degree of impregnation on the resulting 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. The most widely used activation agents[7] 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

2.3.2.2 Physical activation[9,11]

The basic method of activating coal-based granules consists of their treatment with oxidizing gases (steam, carbon dioxide, oxygen) at elevated temperatures. In the activation process, carbon reacts with the oxidizing agent and the resulting carbon oxides diffuse from the carbon surface. Owing to the partial gasification of the granules or grains, a porous structure builds up inside them. The structure of the carbonization product consists of a system of crystallites similar to those of graphite bonded by aliphatic type bonds to yield a spatial polymer. The spaces between the neighbouring crystallites constitute the primary porous structure of the carbon. The pores of the carbonized granules are often filled with tar decomposition products and are blocked with amorphous carbon. This amorphous carbon reacts in the initial oxidation step, and as a result the closed pores open and new ones are formed. In the process of further oxidation, the carbon of the elementary crystallites enters into reaction due to which the existing pores widen. Deep oxidation leads to a reduction in the total volume of micropores due to the burning off of the walls between the neighbouring pores, and in consequence the adsorptive properties and mechanical strength of the material decrease.

In the first stage of activation[12], when burn-off is not higher than 10% (which occurs at low reaction times), this disorganized carbon is burnt out preferentially and the closed and clogged pores between the sheets are freed. In the course of further activation at the second stage, carbon of the aromatic sheets is burnt. 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. Development of macropores due to coalescence or widening of micropores under fast reaction conditions.

Carbon oxidation[9] is a complex heterogeneous process encompassing the transport of reagents to the surface of the particles, their diffusion into the pores, chemisorption on the pore surface, reaction with carbon, desorption of the reaction products, and diffusion of these products to the particle surface. The concentration profile of the oxidizing agent of the granule volume, and hence the formation of the carbon porous structure, depends of the rate of the particular steps of the process. At low temperatures the rate of the chemical reaction of carbon with the oxidizing agent is small, so it is this reaction that limits the overall rate of the process. This results in a dynamic equilibrium becoming established between the concentration of the oxidizing agent in the pores and that in the interparticle spaces. In such a case the activation process yields a homogeneous product with a uniform distribution of the pores throughout the whole volume of the granule. With increase of the oxidation temperature, the rate of the chemical reaction increases much faster than that of diffusion, and then the overall rate of the process becomes limited by the rate of transport of the oxidizing agent into the granule. At very high temperatures the oxidation reaction rate becomes so high that the whole oxidizing agent reacts with carbon on the external surface of the granule. In such a case significant losses of the material occur due to superficial burn-off, and a porous structure is not formed.

The rate of the oxidation process is limited by the reactivity of the initial carbonaceous material towards the oxidizing agent. The greater is the reactivity of the substrates, the lower the optimal temperature of the process at which uniform formation of pores in the granule.

- *Activation with steam* [9,10]

The basic reaction of carbon with water vapor is endothermic and a stoichiometric equation can be written in the form :

$$C + H_2O \longrightarrow H_2 + CO \qquad \Delta H = +130 \text{ kJ/mol}$$

This process has been studied extensively since it dominates not only the activation reaction but also the production of water-gas. The reaction of carbon with water vapor is inhibited by the presence of hydrogen while the influence of carbon monoxide is practically insignificant. The rate of gasification of carbon by water vapor is given by the formula:

$$v = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2O} + k_3 P_{H_2}}$$

where : P_{H_2O} and P_{H_2} are the partial pressures of water and hydrogen, respectively, k_1, k_2, k_3 are the experimentally determined rate constants. The mechanism of reaction of carbon with water vapor can be presented with reasonable confidence by the following set of equations:

$$C + H_2O \rightleftharpoons C(H_2O)$$

$$C(H_2O) \longrightarrow H_2 + C(O)$$

$$C(O) \longrightarrow CO$$

The inhibiting effect due to hydrogen may be assigned to blocking of the active centers by its adsorption.

$$C + H_2 \rightleftharpoons C(H_2)$$

According to Long and Sykes[9] in the first step of the reaction the adsorbed water molecules dissociate according to the scheme :

$$2C + H_2O \longrightarrow C(H) + C(OH)$$

$$C(H) + C(OH) \longrightarrow C(H_2) + C(O)$$

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

The reaction of carbon and water vapor is accompanied by the secondary reaction of carbon monoxide with water vapor (the so-called homogeneous water-gas reaction) catalyzed by the carbon surface:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H = -42 \text{ kJ/mol}$$

Reif [9] explained the presence of carbon dioxide and the catalytic surface effect of carbon by the following reaction :

$$CO + C(O) \rightleftharpoons CO_2 + C$$

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 catalyzed by the oxides and carbonates of alkali metals, iron, copper and other metal; the activation catalyst usually employed in

practice are carbonates of alkali metals, which are added in small amounts to the material to be activated.

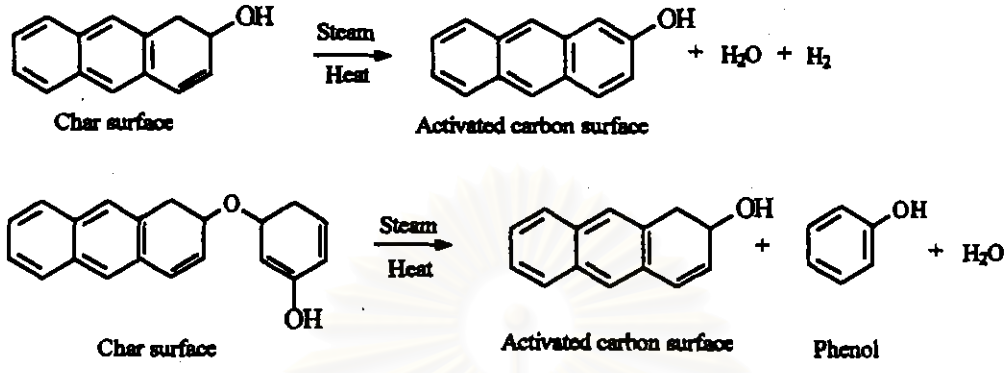

Figure 2.2 Chemical reaction of char with activated by steam[9].

- *Activation with Carbon Dioxide* [9,10]

The rate of carbon gasification with carbon dioxide is described by an expression analogous to that for the reaction with steam :

$$v = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2}}$$

where : P_{CO_2} and P_{CO} are the partial pressures, and k_1, k_2, k_3 are the experimentally determined rate constants. Two different mechanisms of interaction of carbon dioxide with the carbon surface are proposed :

$$(1) \qquad C + CO_2 \longrightarrow C(O) + CO$$

$$C(O) \longrightarrow CO$$

$$CO + C \longrightarrow C(CO)$$

$$(2) \qquad C + CO_2 \longrightarrow C(O) + CO$$

$$C(O) \longrightarrow CO$$

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)* [9,11]

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

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -387 \text{ kJ/mol}$$

$$2C + O_2 \longrightarrow 2CO \qquad \Delta H = -226 \text{ kJ/mol}$$

The used of oxygen as activating agent presents particular difficulties which are due to its exothermic reaction with carbon. In this case it is difficult to avoid local overheating in the activation process. In view of its high rate, the carbon burn-off process proceeds chiefly on the surface of the granules, producing high losses of material. In many processes, oxygen activation is conducted at very low temperatures and combined with treatment with water vapor. Such a method is most convenient when materials of low reactivity are activated.

2.3.3 Pyrolysis and steam activation [13]

Usually the production of activated carbons involves two stages : the carbonization of the raw materials followed by a high temperature activation, at 800-1000°C, of the resulting chars. The method used in this study combines the two stage into a single one, while the treatment temperature is considerably lower, 600-800°C. This method is preferable to the two-stage treatment from an economic point of view. During the pyrolysis and steam activation of carbon-containing materials the following main processes take place:

1. Oxidation-thermolytic conversion of the carbon material leading to the accumulation of oxygen-containing groups.
2. A thermal destruction process including the decomposition of the oxygen-containing groups accompanied by the formation of carbon oxides and water.
3. Condensation processes.
4. Deeper penetration of the water molecules and opening up of the initially closed pores into the structure of the carbon materials.

2.4 Molecular, Crystalline and porous structure of activated carbon [9]

The graphite-like microcrystalline structure is the basic structural unit of activated carbon, as in the case of carbon black. The ordering of carbon atoms in an elementary microcrystallite indicates considerable similarity to the structure of pure graphite, the crystals of which consist of parallel layers of condensed regular hexagonal ring spaced 0.335 nm apart. Such interlayer spacing is diagnostic of interaction by means of van der Waals forces. The length of the carbon-carbon bond in individual layers is 0.142 nm. Each carbon atom bonds with the three adjoining ones by means of covalent bonds, and the fourth delocalized π-electron may move freely in a system of conjugated double bones of condensed aromatic ring. The scheme of arrangement of the carbon atoms in a crystal of graphite is presented in **Figure 2.3.**

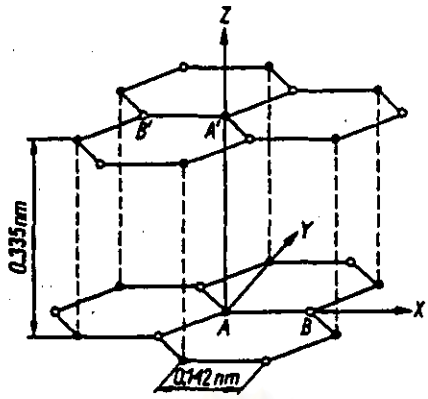

Figure 2.3 Ordering of carbon atoms in a crystal of graphite[9].

The formation of the crystalline structure of activated carbon begins early during the carbonization process of the starting material. Thus sets of condensed aromatic ring of various numbers, which are the nascent centers of graphite-like microcrystallites, are formed. Although their structure resembles that of a crystal of graphite there exist some deviations from that structure. Thus, among other things, the interlayer distances are unequal in crystals of activated carbon and range from 0.34 to 0.35 nm. Again, the orientations of the respective layers generally display deviations. Such deviations from the ordering characteristic of graphite, called a turbostratic structure, are illustrated in **Figure 2.4**. Disordering of the crystal lattice may be caused to a considerable degree both by its defects (vacant lattice sites) and by the presence of built-in heteroatoms. It is resulted from the kind of the raw material used, the nature and quantity of its impurities as well as the methods and conditions of the production processes of the activated carbon.

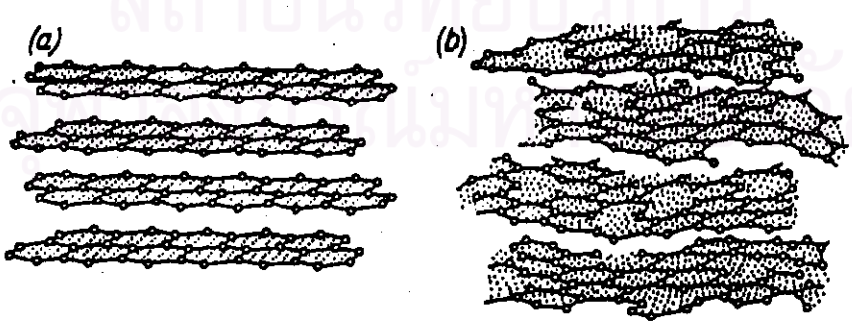

Figure 2.4 Comparison of three-dimensional crystal lattice of graphite (a) and the turbostratic structure (b)[9].

The average activated carbons have a strongly developed internal structure (the specific surface often exceeds 1000 and sometimes even 1500 m^2/g), and they are usually characterized by a polydisperse capillary structure, featuring pores of different shapes and sizes. Bearing in mind the values of the effective radii and the mechanism of adsorption of gases, Dubinin[9] proposed three main types of pore, namely macropores, mesopores and micropores.

Macropores are those having effective radii ≥ 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 cm^3/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 m^2/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.

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 cm^3/g and their specific surface area in the range of 20-100 m^2/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.

Micropores have 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 cm^3/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.

2.5 Chemical nature of the surface of activated carbon [9]

The chemical nature of activated carbons significantly influences their adsorptive, eletrochemical, catalytic, acid-base, redox, hydrophilic-hydrophobic, and other properties. It is determined decisively by type, quantity and bonding of various heteroatoms, especially oxygen. Heteroatoms may be combined both with peripheral carbon atoms at the corners and edges of crystallites, and in intercrystalline spaces and even in defect zones of particular planes constituting the crystallites. Most heteroatoms are grouped at the surface of activated carbon. Apart from their different locations, the heteroatoms are strongly differentiated in terms of their chemical reactivity. Surface-bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds. The surface functional groups often consist of more than one type of heteroatom, e.g. oxygen and hydrogen together as -OH or -COOH.

Surface functional groups can originate from the starting material from which a particular activated carbon is produced. Substantial quantities of oxygen can be introduced during the production process itself, e.g. during activation of carbonaceous materials by oxidizing gases, such as water vapor and air. Activated carbon used predominantly for practical purposes generally includes some percentage by weight of chemically-bound oxygen and usually much smaller quantity of hydrogen combines with surface carbon atoms either directly or through oxygen.

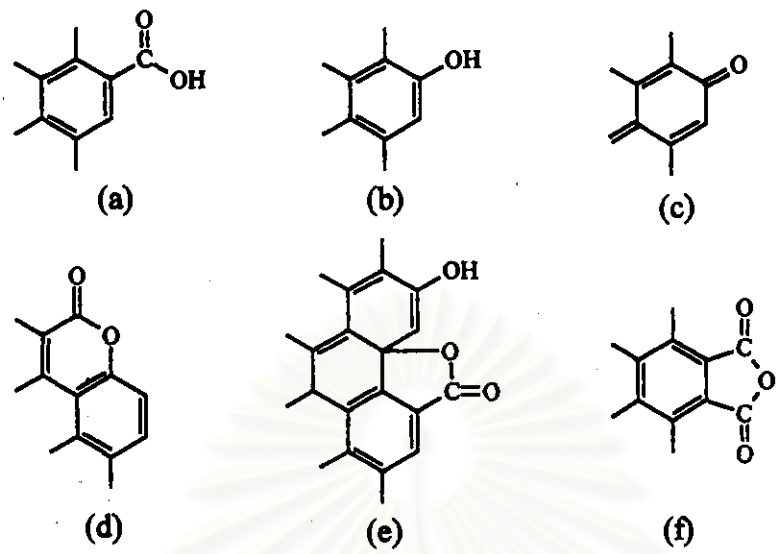

Figure 2.5 Principal types of acidic oxygen surface functional groups : (a) carboxyl, (b) phenolic, (c) quinonoid, (d) normal lactone, (e) fluorescein-type lactone, (f) anhydride originating from neighbouring carboxyl groups[9].

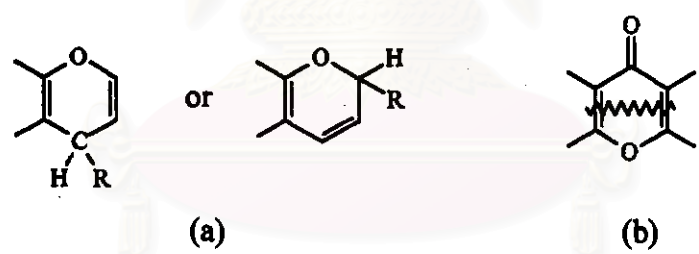

Figure 2.6 Functional groups of basic character : (a) chromene, (b) pyrone-like[9].

Oxygen surface compounds are usually divided into two main types: functional groups of acidic nature and basic groups. The first acidic group is exemplified schematically in **Figure 2.5**. The later basic group is much less well-characterized compared with the first. Usually structures corresponding to chromene or pyrone-like structures are illustrated in **Figure 2.6**.

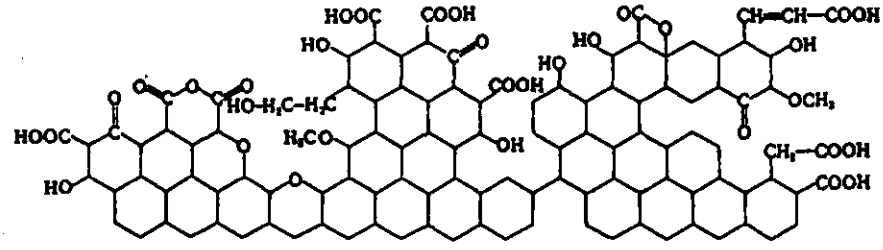

Figure 2.7 Model of fragment of an oxidized activated carbon surface[9].

2.6 Estimation of the properties of activated carbon [9]

The commercial use of activated carbons, their transport, storage and sales require knowledge of the properties of these materials. 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 fur 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.

2.6.1 B.E.T. Surface area [14]

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 into 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/Po 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 on nonporous structures or macroporous materials. Point *B* occurs at a "knee" (**Figure 2.8**) 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.

Type IV is encountered with materials having pores in the general range of 2 to 50 nm (mesopores). At low values of P/Po the isotherm is similar to type II, but then adsorption increases markedly at higher values of P/Po 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/Po. It also relatively rare.

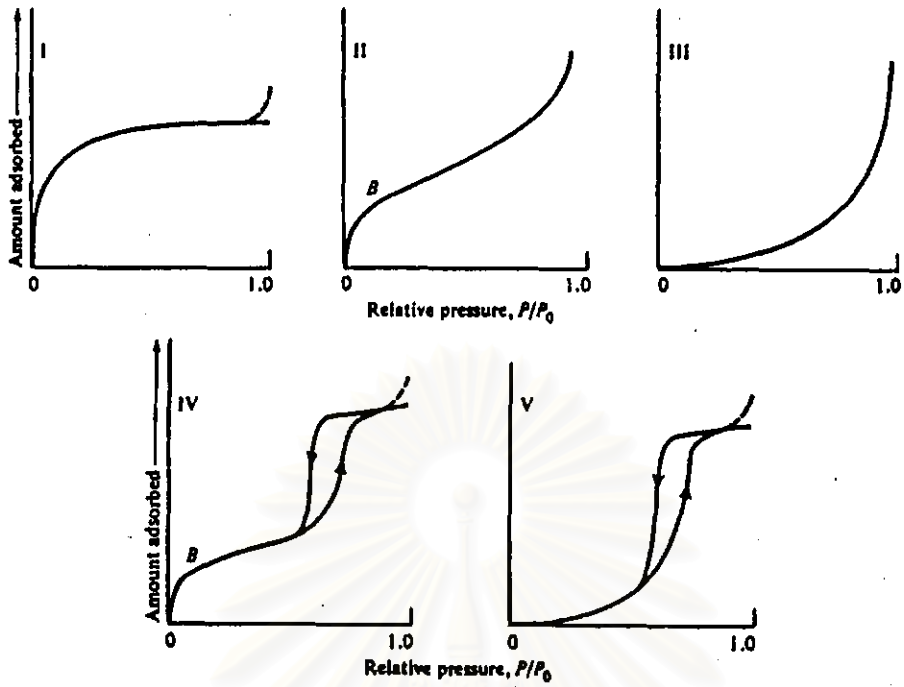

Figure 2.8 The five types of adsorption isotherms[14].

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 layer beyond the first, the rate of adsorption is taken to be proportional to the fraction of the lowest layers 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 :

$$\frac{P}{V(Po-P)} = \frac{1}{V_mC} + \frac{(C-1)P}{V_mCPo} \qquad (2.1)$$

where V = volume of gas adsorbed at pressure P

V_m = volume of gas adsorbed in monolayer, same units as V

Po = saturation pressure of adsorbate gas at the experimental temperature

C = a constant related exponentially to the heats of adsorption and liquefaction of the gas

$$C = e^{(q_1 - q_L)/RT} \quad (2.2)$$

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 (2.1) is obeyed, a graph of P/V(Po-P) versus P/Po 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/Po between approximately 0.05 and 0.3, and this range is usually used for surface area measurements. At higher P/Po 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/Po, typically around 0.01 or less.

2.6.2 Physical test [9]

- *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.

2.6.3 Adsorption tests [9]

The adsorption properties of activated carbons are 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 mesopores of dimensions greater than 1.5 nm.

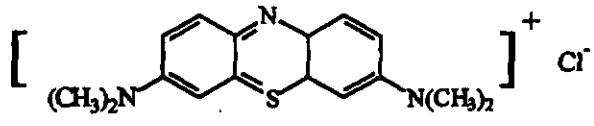

Figure 2.9 The chemical structure of methylene blue[9].

2.6.4 Physico-chemical Test [9]

- *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 nm) activated carbon is heated at 950 ± 25 °C for 7 min ± 10 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, aluminium, 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 ashed carbon is expressed as a percentage of the weight of the original carbon sample.

2.7 Uses of activated carbon [15]

The advantage of using activated carbon is that in certain circumstances a single stage of adsorption may replace several chemical and physical separations or it may permit separation of compounds of the same boiling point. As states earlier, activated carbons are used mainly in the purification and decolorization of liquids and as such are used mostly in powder form and derived from cellulose raw materials (about 85% of total use). Some the advantages of using activated carbon are listed below:

Dry-cleaning solvent. With the increase in dry cleaning in recent years, particularly in coin-operated machines, the need has arisen for a convenient on the spot method of purifying the solvents which with the passage of time because contaminated with oils and grease. These become rancid as well as dark colored and impart obnoxious odors to the cleaning liquid. The odors are reduced but not eliminates by distillation of the solvent. Activated carbon has proved to be effective in decolourizing and deodorizing.

Sugar. The main action of the carbon is in decolorization but it also removes nitrogenous substance and lyophilic colloids. By doing so it improves filtration, reduces foaming during evaporation and increases the speed of crystallization. When saturated the carbon is removed and regenerated by heating in steam and air at a red heat.

Water. Water is usually treated with chlorine to destroy bacteria but this can at times impart an unpleasant taste, which is especially marked when the chlorine has reacted with micro-organisms and with phenol. The bad taste becomes very noticeable when the supplying river is at a low level but it can be removed by treating the water with activated carbon. This should be an increasing market, particularly if the cost of activated carbon can be reduced.

Tyres. It has been found that white wall tyres retain their whiteness better if activated carbon is incorporated in the reinforcing carbon black.

Pharmaceuticals. Activated carbon has the property of concentrating the active component from a broth. The desires component can be recovered from the carbon by solvents. Penicillin was the first to be treated on a large scale by this method. With the increasing emphasis being placed on pollution by effluents it would seem that activated carbon may play an important part in reducing this problem.

Foodstuffs. Here activated carbons are used to remove soaps and peroxides from edible fats to prevent poisoning of hydrogenation catalysts. They also improve color and flavour, e.g. in soup stocks and vinegar, and improve the storage properties of freshly distilled whisky.

Gas phase carbons. These should have the following properties : (i) high absorptive capacity; (ii) high retention; (iii) high selectivity in the presence of water vapor; (iv) low flow resistance; (v) high resistance to breakage; (vi) complete release of vapor at increased temperature and decreased pressure. They have two main applications :

- Gas purification, as for example in the recovery of raw gasoline from natural gas; in air conditioning, to remove cooking smells and body odours; as emergency traps against the accidental emission of radioactive gases. Much attention has been paid recently to the removal of the oxides of sulfur from combustion gas e.g. at

thermal power stations. Activated carbon has been tried for this purpose and while effective in removing SO_2, it produces a dilute solution of sulfuric acid which would require concentrating before it was of value.

- Catalysis, as for example in the oxidation of H_2S to sulfur. In order to prevent deposition in the pores of the carbon, this process is best carried out at high temperatures. Generally, activated carbon is used more as a catalyst support than as a catalyst in its own right.

2.8 Literature reviews

Gergova *et al.* (1993)[13] used a one step pyrolysis/steam activation to produce activated carbon from apricot stones, nuts, coconuts, almond shells and grape seeds, and Bulgarian lignite from Maritza lztok and Chukurovo deposit. The 50 g sample was heated in a tube furnace at a heating rate 10°C/min, at atmospheric pressure and steam at a flow rate of 0.5 dm^3/hr. The experiments were carried out in a temperature range of 600-700 °C. The samples were heated at the final temperature for 1, 2 and 3 hr. The activated carbon produced from various raw materials had high concentration of functional groups, hydroxyl and carbonyl. In summary, the differences in the structure of the raw materials led to the formation of different oxygen-containing groups on the resulting activated carbon surfaces due to their reaction with water molecules. The adsorption properties of activated carbon were dependent on the treatment temperature, soak time and the nature of the raw materials. The activated carbon produced from apricot stones at 700°C for 2 hr had the highest surface area (1175 m^2/g). The total pore volume and surface area of activated carbon from coal and agricultural by-products are shown in **Table 2.1.**

Table 2.1 Total pore volume and surface area of activated carbon from coal and agricultural by-products[13].

Activated carbon precursor	$S_{B.E.T.}$ (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{macro} (cm^3/g)
Apricot stones	1175	0.91	0.76	0.14	0.01
Grape seeds	487	0.62	0.16	0.22	0.24
Almond shells	946	0.60	0.21	0.17	0.22
Nut shells	904	0.55	0.13	0.35	0.07
Coconut shells	700	0.46	0.20	0.14	0.12
Lignite Maritza Iztok	600	0.98	0.07	0.32	0.59

Gergova, Petrov and Minkova (1993)[16] produced activated carbon from apricot stones, grape seeds and cherry stones by a new one-step steam/pyrolysis activation which combined the process of carbonization and activation with water vapor. The experiments had been carried out at temperatures of 600, 650 and 700°C and soak time 1, 2 and 3 hr. The adsorption and porosity characteristics of the activated carbon produced from different agricultural by-products are shown in **Table 2.2** .

Table 2.2 Adsorption and porosity characteristics of the activated carbons produced from different agricultural by-products[17].

Raw material	Yield (wt%)	$S_{B.E.T.}$ (m^2/g)	IA (mg/g)	MB (mg/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{macro} (cm^3/g)
Apricot stones	18.16	1175	894	285	0.91	0.76	0.14	0.01
Grape seeds	26.23	487	607	192	0.62	0.16	0.22	0.24
Cherry stones	11.17	836	907	185	0.77	0.20	0.09	0.48

Activated carbon obtained from apricot stones had the best properties. It was characterized to have a large specific surface area and micropores volume and high iodine and methylene blue adsorption activity. The activated carbon was produced from cherry stones and grape seeds, had predominating meso- and macropores structure.

Budinova *et al.* (1994)[17] studied the adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} from aqueous solution at 293 K by activated carbon obtained from different raw materials. The activated carbon was prepared by a simple single-stage method "pyrolysis in the presence of water vapor" (PPWV) of apricot stones, coconut shells and lignite coal. The results presented that all activated carbon (PPWV) had an ability to adsorb metal ions from aqueous solution with the capacity increasing in the order $Cd^{2+} < Zn^{2+} < Cu^{2+} < Pb^{2+}$. The adsorption of metallic ions was negligible at low pH values and increased considerably in the pH range of 3-4.

Boonchai Thakunmahachai (1994)[18] produced activated carbon from palmyra palm shells by physical or chemical method. The physical activation in the fluidized bed and the chemical activation in the fixed bed were studied. In order to get the charcoal which could be grinded easily, the palmyra palm shells were carbonized at temperature of 200°C for 2 hr. The sample of charcoal was mixed with the solution of 60% (wt) zinc chloride at the ratio of 3 : 2 in the porcelain crucible for 72 hr. The optimum condition for the charcoal particle size of 1.68-2.38 mm was at 500°C activation temperature for 1 hr. The properties of the activated carbon was 1600-1700 m^2/g surface area, 1100-1200 mg/g iodine adsorption, 350-400 mg/g methylene blue adsorption, 2-5% ash and 40-45% yield. The palmyra palm shells were physically activated with the mixed gas of flue gas which had been obtained from diesel oil and superheated steam in fluidized bed. The optimum condition for charcoal particle size of 1.19-1.68 mm was at activation temperature of 900°C for 5 min and gas velocity of 6.44 m/sec. The properties of activated carbon were 1800-1900 m^2/g surface area, 1000-1300 mg/g iodine adsorption, 250-350 mg/g methylene blue adsorption , 10-15% ash and 30-45% yield.

Arriagada, Gercia and Reyes (1994)[19]: The partial gascification of *Eucalyptus globulus* charcoal, using carbon dioxide and steam as activating agents was studied. The influence of some production variables such as temperature and reaction time on textural were given. *Eucalyptus globulus* chips (5-10 cm in diameter, 30-40 cm in length) were carbonized in a metallic kiln. The carbonization time was 2-3 hr and the yield of charcoal was 23%. The charcoal, sieved between 10 and 20 mesh was activated in a vertical fixed bed reactor. The reaction temperature between 800-900°C for 10-360 min with flow of the activating agent was 200 cm^3/min (STP) of carbon dioxide or 140 cm^3/min (STP) of steam (100%). The results showed that both activating agents produced microporous activated carbon with a large increase in meso- and macroporosity when steam and high burn-off were used. **Table 2.3** summarizes the textural characteristics of the activated carbon.

Table 2.3 Textural characteristics of the activated carbon[19].

Activating agent	Time (min)	Surface area (m^2/g)	IA (mg/g)	MB (mg/g)
CO_2	10	380	286	16
	60	549	474	84
	120	678	640	125
	180	847	725	220
	270	994	929	318
	360	1089	936	345
Steam	10	466	471	14
	60	622	690	113
	120	778	819	221
	270	1193	968	311

Gergova, Klimkiewicz and Brown (1995)[20] : Experiments were carried out the production of activated carbon from anthracite using one-step steam pyrolysis-activation. The 50 g of anthracites were heated in a tube furnace for pyrolysis-activation at a rate of 20 K/min at atmospheric pressure. The samples, with particle size < 1 mm, were heated in the presence of steam at 850°C for 3-6 hr and at 900°C for 3 and 4 hr at atmospheric pressure. Two samples were treated initially in air at

300 and 350°C for 3 and 2 hr, followed by steam activation at 850°C for 4 hr. The activated carbon produced by steam activation at 850°C for 6 hr had the highest surface area and a well-developed porous structure. Substantial activation of anthracite surfaces and formation of extensive porosity occurred under the same conditions but with steam at 270 Pa instead of atmospheric pressure. Air treatment at 300°C for 3 hr before steam activation at 850°C for 4 hr also led to production of activated carbon with well-developed porosity. The porosity characteristics of activated carbon from anthracite are shown in **Table 2.4.**

Table 2.4 Porosity characteristics of activated carbon from anthracite[20].

Air flow		Steam flow			Surface area (m^2/g)				Pore volume (cm^3/g)	
T (°C)	t (hr)	T (°C)	t (hr)	Yield (wt%)	$S_{B.E.T.}$	L(h)*	D-R*	IA	Total	Micro
300	3	850	4	37.2	720	1420	1310	620	0.56	0.34
350	2	850	4	36.0	670	1340	1230	650	0.53	0.32
-	-	850	3	45.8	530	1130	950	470	0.42	0.25
-	-	850	4	31.2	610	1280	1130	580	0.48	0.29
-	-	850	5	28.4	630	1310	1150	610	0.50	0.30
-	-	850	6	25.3	720	1460	1360	540	0.57	0.35
-	-	900	3	23.6	620	1280	1180	620	0.49	0.30
-	-	900	4	13.5	510	1120	1050	450	0.40	0.24

* Langmuir (high relative pressure) * Dubinin-Radushkevich

Hussein *et al.* (1995)[21] prepared the activated carbon by $ZnCl_2/CO_2$ activation of the chips of oil palm trunk. Ten grams of the air-dries chips of oil palm trunk were mixed with 100 cm^3 of 1-30% (w/w) $ZnCl_2$ and activated at 500°C under an inert flow of nitrogen gas for 3 hr. After this time, CO_2 was passed through the reactor for an hour. Activated carbon prepared by impregnation of 0-10% of $ZnCl_2$ had a microporous structure. Introduction of 15% (or more) $ZnCl_2$, however, had modified the pores of the resulting activated carbon to include a mesoporous structure. An optimum micropore volume occured at 5 % $ZnCl_2$.

Thus, it was believed that at high concentrations of $ZnCl_2$, a relatively large portion of $ZnCl_2$ could modify some of the original micropores to mesopores. This experimental method could be used to production of activated carbon with a fairly high surface area more than 2000 m^2/g from the chips of oil palm trunk.

Tancredi *et al.* (1996)[22] prepared activated carbon from eucalyptus wood chars. The results of CO_2, CO_2-O_2 and steam activation were compared. The sawdust of eucalyptus 0.5-1.6 mm was first carbonized in a continuous N_2 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 CO_2, steam and CO_2-O_2 mixtures as activating agents. Activated carbon was obtained, by CO_2 activation of the 800°C chars with surface area of 780 up to 1190 m^2/g and 810 up to 1190 m^2/g, when steam activation at 800°C. The carbonization step gave rise to a narrow micropore structure and highly developed macroporosity which increased slightly upon CO_2 activation and significantly upon steam activation. This last process led also to a widening of micropore size distribution and developed the mesoporosity more than CO_2 activation did. Steam activation appears to have a particularly relevalent effect on macroporosity development. As steam had a higher reactivity than CO_2, 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 of steam activation temperature. The presence of O_2 accompanying CO_2 in the activating gas small increased the micro- and macroporosity of the carbons, compared with pure CO_2 activation.

Philip and Girgis (1996)[23]: The apricot stone shells were impregnated with varying H_3PO_4 acid concentrations (20-50 wt%, followed by carbonization at 300-500 °C for 3 hr in a closed-end quartz tube reactor. A series of wide range micropores of activated carbon were obtained, with surface area of 640 up to 1600 m^2/g, pore volumes of 0.34 up to 1.32 cm^3/g and mean pore radii of 7.8-20.2 Å.

Sai *et al* (1997)[24] produced activated carbon from coconut shell 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 CO_2 or pure CO_2. 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 shell char.

Patra Panyawatanakit (1997)[25] produced activated carbon from palm oil shells. The processes of carbonization and activation with superheated steam were studied. Some of the characteristics of palm-oil shells were found to be : moisture of 11.87 %, ash of 2.20 %, volatile matter of 69.87 %, fixed carbon of 16.06 % , total surface area of 12.20 m^2/g, mesopore area of 12.20 m^2/g and micropore area of 0.00 m^2/g. The palm-oil shells were carbonized at 400°C for 1 hr. The characteristics of the palm-oil shell charcoal were yield of 31.50 %, ash of 6.24 %, volatile matter of 27.76 %, fixed carbon of 64.48 %. Next, the charcoal was activated with superheated steam. The optimum condition for activation was 0.850-0.355 mm of charcoal size at 900°C for 1 hr. The resulting characteristics were yield of 19.31 %, bulk density of 0.53 g/cm^3, iodine number of 779.0 mg/g, methylene blue number of 136.96 mg/g, total surface area of 670.1 m^2/g, mesopore area of 67.24 m^2/g, micropore area of 602.8 m^2/g and average pore area of 10.11 Å.