

CHAPTER II

THEORY AND LITERATURE REVIEW



2.1 Activated carbon⁽⁶⁾

Activated carbon⁽⁶⁾ is a processed carbon material with a highly developed porous structure and a large internal specific surface area. To 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 streams, 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.

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 absorptive conditions (temperature, pressure, or concentration) more or less completely regenerates the carbon activity, and frequently allows recovery of both the carrier fluid and adsorbent. Compared with other commercial adsorbents, activated carbon has a broad spectrum of absorptive 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-absorbent 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.

2.2 Raw materials for the production of activated carbon^(6,7)

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. Sources of materials that have been studied for the production of activated carbon are listed as followed.

Bagasse	Corncobs and corn	Leather waste	Petroleum acid sludge
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
Beet-sugar sludges	Stalks		

2.3 Production of activated carbon

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

2.3.1 Carbonization (or pyrolysis) ⁽⁶⁾

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. 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 free 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 tar 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 27-197⁰C range; (b) primary pyrolysis in the 197-497⁰C range with evolution of most gases and tars with formation of the basic structure of the char; (c) consolidation of char structure at 497-847⁰C 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 (400-600⁰C), 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^(6,7)

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

2.3.2.1 Chemical activation

For chemical activation^(6,7,8), 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.

Chemical activation⁽⁸⁾ 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 (coefficient) 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. 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⁽⁸⁾ are :

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

2.3.2.2 Physical activation^(7,9)

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 neighboring 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 neighboring pores, and in consequence the adsorptive properties and mechanical strength of the material decrease.

In the first stage of activation⁽⁸⁾, 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 unde fast reaction conditions.

Carbon oxidation¹⁶⁾ 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 inter particle 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 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 ^(6.7)

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



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:

$$V = \frac{k_1 P_{\text{H}_2\text{O}}}{1 + k_2 P_{\text{H}_2\text{O}} + k_3 P_{\text{H}_2}}$$

Where : $P_{\text{H}_2\text{O}}$ 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:



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

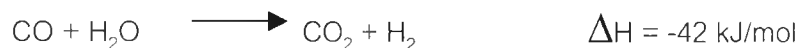


According to Long and Sykes⁽⁸⁾ in the first step of the reaction the adsorbed water molecules dissociate according to the scheme :



Hydrogen and oxygen are adsorbed at neighboring 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 :



Reif⁽⁶⁾ explained the presence of carbon dioxide and the catalytic surface effect of carbon by the following reaction :



Activation with steam is carried out at temperatures from 750 to 950⁰C 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. It was shown in Figure 2.1.

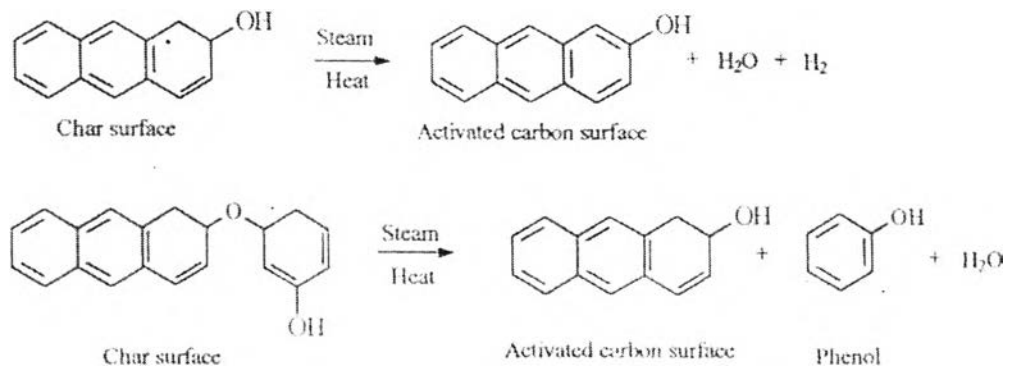


Figure 2.1 Chemical reaction of char with activated by steam⁽⁸⁾

-Activation with carbon dioxide^(7,8)

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. Two different mechanisms of interaction of carbon dioxide with the carbon surface are proposed :



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 is carbonates of alkali metals.

-Activation with oxygen (air)^(8,9)

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



The using 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⁽⁸⁾

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. The scheme of arrangement of the carbon atom is presented in Figure 2.2.

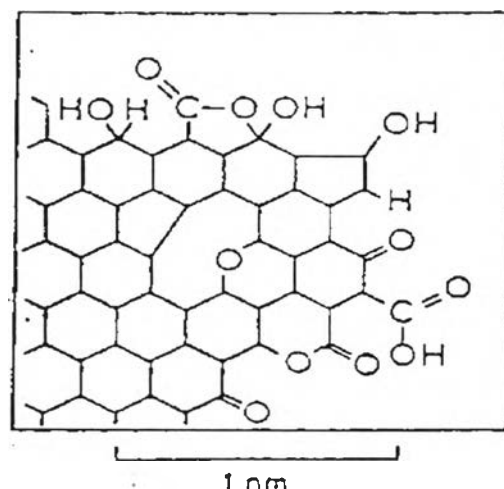


Figure 2.2 Ordering of carbon atoms ⁽⁸⁾

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 carbon materials.

2.4 Molecular, crystalline and porous structure of activated carbon ⁽⁶⁾

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 bonds of condensed aromatic ring.

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 "*turbostatic structure*". 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.

The average activated carbons have a strongly developed internal structure (the specific surface often exceeds 1,000 and sometimes even 1,500 m²/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⁽⁸⁾ proposed three main types of pore, namely macropores, mesopores and micropores.

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 type 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 take place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.1-0.50 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.

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 cm³/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the nonporous 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. It is showed in Figure 2.3

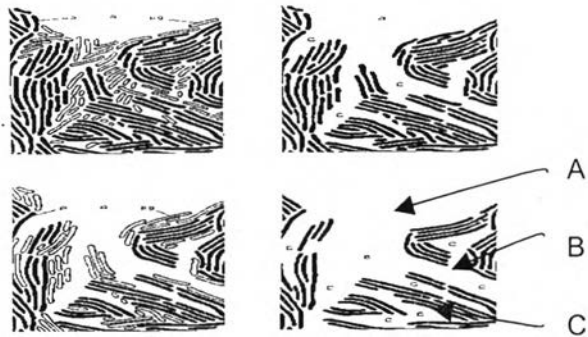


Figure 2.3 Porous structure of activated carbon.

A: macropore B: mesopore C: micropore.

2.5 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 Method 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.

2.5.1 B.E.T. Surface area⁽⁶⁾

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/P_0 approaches unity.

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 :

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (2.5.1)$$

- 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

$$C = e^{(q_1 - q_L)/RT} \quad (2.5.2)$$

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 (2.5.1) and (2.5.2) are 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⁽⁶⁾

-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⁽¹⁰⁾

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.

2.5.4 Physico-chemical Test⁽¹⁰⁾

-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 $7 \text{ min} \pm 10$ 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 off 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 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.

2.6 Uses of activated carbon ^(11,12)

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 stated earlier, activated carbons are used mainly in the purification and decolorization of liquids and

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 become 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 eliminated by distillation of the solvent. Activated carbon has proved to be effective in decolorizing 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 desired 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 flavor, 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 odors; 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 SO₂, 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 H₂S 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.

2.7 Literature reviews

Torikai et al. (1979)⁽¹⁶⁾ 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.

Gergova et al. (1993)⁽¹⁷⁾ 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 Iztok and Chukurovo deposit. The 50 g sample was heated in a tube furnace at a heating rate $10^{\circ}\text{C}/\text{min}$, at atmospheric pressure and steam at a flow rate of $0.5 \text{ dm}^3/\text{hr}$. The experiments were carried out in a temperature range of $600\text{-}700^{\circ}\text{C}$. 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 ($1,175 \text{ m}^2/\text{g}$). 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.⁽¹⁷⁾

Activated carbon Precursor	$S_{\text{B.E.T.}}$ (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

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 grind 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 m²/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 m²/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⁾ studied the partial gascification of Eucalyptus globules charcoal, using carbon dioxide and steam as activating agents. The influence of some production variables such as temperature and reaction time on textural were given. Eucalyptus globules 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 cm³/min (STP) of carbon dioxide or 140 cm³/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 2.2 summarizes the textural characteristics of the activated carbon.

Table 2.2 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⁾ carried out the production of activated carbon from anthracite using one-step steam pyrolysis activation at a rate of 20K/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 Table2.3.

Table 2.3 Porosity characteristics of activated carbon from anthracite⁽²⁰⁾

Air flow		Steam flow		Yield (wt%)	Surface area (m ² /g)				Pore volume (cm ³ /g)	
T (°C)	t (hr)	T (°C)	t (hr)		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
-	-	850	3	23.6	620	1280	1180	620	0.49	0.30
-	-	850	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 ZnCl₂/CO₂ activation of the chips of oil palm trunk. Ten grams of the air-dry chips of oil palm trunk were mixed with 100 cm³ of 1-30% (w/w) ZnCl₂ and activated at 500 °C under an inert flow of nitrogen gas for 3 hr. After this time, CO₂ was passed through the reactor for an hour. Activated carbon prepared by impregnation of 0-10% of ZnCl₂ had a microporous structure. Introduction of 15% (or more) ZnCl₂, however, had modified the pores of the resulting activated carbon to include a mesoporous structure. An optimum micropore volume occurred at 5% ZnCl₂. Thus, it was believed that at high concentrations of ZnCl₂, a relatively large portion of ZnCl₂ could modify some of the original micropores to mesopores. This experimental method could be used to producing of activated carbon with a fairly high surface area more than 2000 m²/g from the chips of oil palm trunk.

Tancredi et al. (1996)⁽²²⁾ prepared activated carbon from eucalyptus wood chars. The results of 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 was obtained, by CO₂ activation of the 800 °C chars with surface area of 870 up to 1190 m²/g and 810 up to 1190 m²/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 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. Steam activation appears to have a particularly relevant effect on macroporosity development. As steam had a higher reactivity than CO₂, diffusion 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 O₂ accompanying CO₂ in the activating gas small increased the micro- and macroporosity of the carbons, compared with pure CO₂ activation.

Sai et al (1997)⁽²³⁾ 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 CO₂ or pure CO₂. From the experimental data, it was observed

that maximum iodine number could be 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, as coconut shell char.

Panyawatanakit (1997)⁽²⁴⁾ 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 m²/g, mesopore area of 12.20 m²/g and micropore area of 0.00 m²/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/cm³, iodine number of 779.0 mg/g, methylene blue number of 136.96 mg/g, total surface area of 670.1 m²/g, mesopore area of 67.24 m²/g, micropore area of 602.8 m²/g and average pore area of 10.11 Å.

Suravattanasakul(1998)⁽²⁵⁾ produced activated carbon from palm-oil shells by one step pyrolysis and steam activation in a fixed bed reactor with the diameter of 100 mm. The studied variables were temperature, time, palm-oil shells size and flow rate of air. The results showed that the optimum condition was 1.18-2.36 mm of palm-oil shells at 750 °C for 2 hr with air flow rate of 0.72 ml/min, using steam as an activating agent. The characteristics of the resulted activated carbon with the yield of 19.66% were bulk density of 0.5160 g/cm³, 6.03% ash, iodine number of 620.16 mg/g, methylene blue number of 176.75 mg/g and 559.48 m²/g B.E.T. surface area. When there was an addition of pyrolysis time with air before steam activation led to higher porosity development than one step pyrolysis and steam activation. From these experimental data, it was observed that the maximum surface area and adsorption capacity could be obtained from using 200 g of 1.18-2.36 mm of palm-oil shells at 750 °C for 3 hr by

adding pyrolysis with air for 30 min (0.72 ml/min) before steam activation. The resulting characteristics of the final product with the yield of 12.18% were bulk density of 0.5048 g/cm³, 7.54% ash, iodine number of 766.99 mg/g, methylene blue number of 189.20 mg/g and 669.75 m²/g B.E.T. surface area.

Sopanakijkosol (2000)⁽¹⁴⁾ produced activated carbon from coconut shells for removing chromium (VI) from industrial wastewater by activation with H₃PO₄. The optimum process conditions for carbonization and activation such as temperature and time were determined. The properties of activated carbons, i.e., iodine number, specific surface area and functional groups were analyzed. The results show that the optimum condition for carbonization was 400 °C for 1 hour and the optimum condition for activation was 800 °C for 2 hours. The BET surface areas and iodine number were found to be 922 m²/g and 1,015 mg/g, respectively. Thus, the result shows much higher adsorption capacity for chromium (VI) comparison with commercial activated carbon.