THE PRODUCTION AND CHARACTERIZATION OF ACTIVATED CARBON USING LOCAL AGRICULTURAL WASTE THROUGH CHEMICAL ACTIVATION PROCESS

by

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%	Percentage of weight
K	Kelvin
˚C	Celcius
nm	nanometer (1x 10^{-9})
cm^3	centimeter cubic
m^2/g	meter square per gram
Ǻ	Angstron (1x 10^{-10})
Kg/m^3	Kilogram per meter cubic
g/mol	Gram per mol
mm	Millimeter
mg	Milligram
cm	Centimeter
g/l	Gram/liter
ppm	part per million
M	Molar
mg/g	milligram/gram
v	vibration

LIST OF ABBREVIATIONS

AC	Activated Carbon
ASTM	American Standard Test Method
BSU	Basic strucure unit
BET	Brunauer-Emmett-Teller
CS	Coconut shell
CSZ	Activated carbon from coconut shell with zinc chloride activation
CSH	Activated carbon from coconut shell with phosphoric acid activation
CSZ1M	Activated carbon from coconut shell with zinc chloride activation at 1 M concentration
CSZ3M	Activated carbon from coconut shell with zinc chloride activation at 3 M concentration
CSZ5M	Activated carbon from coconut shell with zinc chloride activation at 5M concentration
CSZ300	Activated carbon from coconut shell with zinc chloride activation at 300°C activation temperature
CSZ400	Activated carbon from coconut shell with zinc chloride activation at 400°C activation temperature
CSZ500	Activated carbon from coconut shell with zinc chloride activation at 500°C activation temperature
CSZ060	Activated carbon from coconut shell with zinc chloride activation at 60 minute activation time
CSZ060	Activated carbon from coconut shell with zinc chloride activation at 60 minute activation time
CSZ120	Activated carbon from coconut shell with zinc chloride activation at 120 minute activation time
CSZ180	Activated carbon from coconut shell with zinc chloride activation at 180 minute activation time
CSH10	Activated carbon from coconut shell with phosphoric acid activation at 10 % concentration
CSH020	Activated carbon from coconut shell with phosphoric acid activation at 20 % concentration

CSH030	Activated carbon from coconut shell with phosphoric acid activation at 30 % concentration
CSH040	Activated carbon from coconut shell with phosphoric acid activation at 40 % concentration
CSH300	Activated carbon from coconut shell with phosphoric acid activation at 300°C activation temperature
CSH400	Activated carbon from coconut shell with phosphoric acid activation at 400°C activation temperature
CSH500	Activated carbon from coconut shell with phosphoric acid activation at 500°C activation temperature
CSH060	Activated carbon from coconut shell with phosphoric acid activation at 60 minutes activation temperature
CSH120	Activated carbon from coconut shell with phosphoric acid activation at 120 minutes activation temperature
CSH180	Activated carbon from coconut shell with phosphoric acid activation at 180 minutes activation temperature
FTIR	Fourier Transform Infrared Spectrophotometer
min	Minute
PS	Palm kernel shell
PSH	Activated carbon from coconut shell with phosphoric acid activation
PSZ	Activated carbon from palm kernel shell with zinc chloride activation
SEM	Scanning electron microscopy

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LIST OF PUBLICATIONS AND SEMINARS

1.1 Characterization of Activated Carbon Prepared From Coconut Shell By Zinc Chloride Impregnation At Different Stages

1.2 Physical and Chemical Properties of Activated Carbon from Coconut Shell

PENGHASILAN DAN PENCIRIAN KARBON TERAKTIF MENGGUNAKAN BAHAN BUANGAN PERTANIAN TEMPATAN MELALUI PROSES PENGAKTIFAN KIMIA

ABSTRAK

Karbon teraktif daripada tempurung kelapa dan tempurung kelapa sawit telah berjaya dihasilkan melalui proses pengaktifan kimia dengan menggunakan zink klorida dan asid fosforik sebagai agen pengaktif. Kesan suhu pengaktifan, masa pengaktifan dan kepekatan agen pengaktif terhadap luas permukaan BET, morfologi permukaan dan hasil (berat kering) telah dikaji. Keputusan menunjukkan di dalam semua kes, peningkatan suhu pengaktifan dari 300˚C hingga 500˚C dan masa pengaktifan dari 60 minit hingga 180 minit menyebabkan peratus hasil menurun, manakala luas permukaan meningkat. Nilai luas permukaan karbon teraktif tertinggi diperolehi dengan menggunakan 5 M kepekatan zink klorida dan 30% kepekatan larutan asid fosforik iaitu 893 m^2/g dan 833 m^2/g masing-masing. Oleh itu, suhu optimum yang diperolehi adalah pada 500˚C dan masa pengaktifan yang diperlukan adalah 120 minit. Pencirian ke atas karbon teraktif dilakukan dengan memilih empat sampel yang dihasilkan dari kedua-dua jenis bahan mula (CS & PS) pada suhu, masa dan kepekatan yang optimum (CSZ, PSZ, CSH, PSH). Keputusan analisis unsur menunjukkan kandungan karbon di dalam sampel adalah lebih daripada 75% manakala kandungan nitrogen dan sulfur adalah kurang dari 0.1%. Manakala, kandungan karbon tetap bagi karbon teraktif yang dihasilkan adalah di antara 54% hingga 79% dan kandungan bahan meruap yang tinggal adalah dari 11% hingga 36%. Kandungan peratus lembapan pula adalah kurang daripada 10% dan akhir sekali nilai abu akhir adalah kurang dari 2%. Analisis FTIR menunjukkan bahawa kumpulan hidroksil, karbonil, alifatik, eter, alkohol, fenol dan kumpulan karbosilik dapat dikesan pada permukaan kedua-dua bahan mula. Setelah proses pengaktifan dan pengkarbonan, keputusan menunjukkan bahawa terdapat kumpulan berfungsi baru yang terbentuk seperti karbon-aromatik dan polifosfat-ester pada karbon teraktif yang dihasilkan dan beberapa kumpulan berfungsi telah disingkirkan seperti karbosilik, alkohol dan karbonil. Ujian keupayaan penjerapan telah dijalankan keatas karbon teraktif yang dihasilkan menggunakan kaedah pentitratan nombor iodin. Keputusan menunjukkan bahawa nilai nombor iodin yang tinggi telah diperolehi bagi sampel CSZ dan PSZ iaitu pada 966 mg/g dan 959 mg/g masing –masing. Kajian keberkesanan penyingkiran sianida telah dijalankan untuk menentukan potensi penggunaan karbon teraktif yang dihasilkan. Peratus penyingkiran sianida berjaya diperolehi lebih daripada 98% pada kepekatan awal sianida 25 mg/l dengan menggunakan 0.5 g karbon teraktif yang dihasilkan dari tempurung kelapa sawit melalui pengaktifan dengan asid fosforik yang telah di jerap-isi dengan 5 % larutan kuprum sulfat. Bagi karbon teraktif yang tidak dijerap-isi, keputusan menunjukkan peratus penyingkiran sianida adalah kurang dari 60% pada kepekatan awal sianida 25 mg/l dan 50 mg/l. Daripada ujian penyingkiran sianida, ia menunjukkan bahawa karbon teraktif yang dihasilkan daripada tempurung kelapa dan tempurung kelapa sawit boleh digunakan sebagai penjerap dalam perawatan air sisa sianida.

THE PRODUCTION AND CHARACTERIZATION OF ACTIVATED CARBON USING LOCAL AGRICULTURAL WASTE THROUGH CHEMICAL ACTIVATION PROCESS

ABSTRACT

Activated carbon from coconut shell and palm kernel shell has been successfully produced through chemical activation process using zinc chloride and phosphoric acid as activating agents. The effect of activation temperature, activation time and concentration of activating agent on BET surface area, surface morphology and yield (dry weight basis) were studied. The result showed that in all cases, increasing the activation temperature from 300˚C to 500 ˚C and activation time from 60 to 180 minutes caused a decrease in the percentage yield while the BET surface area is increased, progressively. The highest BET surface area of the activated carbon obtained by using 5 M zinc chloride concentration and 30% concentration of phosphoric acid is 893 m^2/g and 833 m^2/g respectively. Hence, the optimum temperature for production of activated carbon was obtained at 500˚C and optimum activation time was obtained at 120 minutes. Characterization of the activated carbon produced was done by selecting four samples from both the raw materials (CS & PS) at optimum temperature, activation time and concentration (CSZ, PSZ, CSH, PSH). Elemantal analysis showed that carbon content in the samples is high which is over 75% and the nitrogen and sulphur content is less than 0.1%. While, the fixed carbon of activated carbon produced is in the range of 54% to 79% and the volatile matter left is from 11% to 36%. The moisture content is less than 10% and finally ash content is less than 2% for all samples selected. FTIR analysis showed the hydroxyl, carbonyl, aliphatic, ethers, alcohol, phenol and carboxylic groups are present on the surfaces of both the raw materials.

After the activation and carbonization process, the new functional groups were assigned such as carbon-aromatic groups and polyphosphate esters on activated carbon produced and some of the functional groups were eliminated such as carboxylic, alcohol and carbonyl. The adsorption capacity test of the produced activated carbon was determined by iodine number. The highest iodine number obtained from CSZ and PSH samples are 966 and 959 mg/g respectively. The cyanide removal efficiency was carried out to determine the potential application of produced activated carbon. The percentage of cyanide removal is successfully obtained more than 98 % at initial cyanide concentration of 25 mg/l by using 0.5g of activated carbon produced from palm kernel shell through phosphoric acid activation (PSH) impregnated with 5 % of copper from $Cu(II)SO_4$ solution. For raw activated carbon (non-impregnated AC), the results showed a lower cyanide removal of below 60 % at initial cyanide concentration of 25 mg/l and 50 mg/l. From the cyanide removal test, the activated carbon produced from coconut shell and palm kernel shell by chemical activation can be used as an adsorbent in cyanide waste water treatment.

CHAPTER ONE
INTRODUCTION

1.1 Background

Recently, carbon has been one of the magnificent elements which have revolutionized material science. From carbon we obtain the best porous absorber (activated carbon) with excellent properties for large spectrum of industrial applications. Activated Carbon (AC) is the common term used for a group of absorbing substances of crystalline form, having a large internal pore structures that make the carbon more absorbent (Strand, 2001). These properties are obtained when a char is subjected to controlled gasification by oxidizing gases, or when a raw material impregnated with dehydrating agents is subjected to carbonization.

Generally, the raw materials for the production of AC are those with high carbon but low inorganic contents such as wood, lignite, peat and coal (Lua and Guo, 2001). Beside that, lot of agricultural waste and by product have successfully converted to AC for examples macadamia nutshell (Ahmadpour and Do, 1996), paper mill sludge(Khalili, et al., 2000) and peach stones (Arriagada, et al., 1997). In Malaysia there are potential raw materials resources for the production of the activated carbon. In this research, two local agricultural waste which are coconut shells and palm kernel shells were used to produce an activated carbon due to the availability and inexpensive material with high carbon and low inorganic content. A number of researches have been reported in the literature using coconut shell and palm kernel shell as a raw materials. Table 1.1 summarizes various works with reference to the raw materials using, methods and their application of AC produced.

Table 1.1 Summary of earlier work on activated carbon using coconut shell and palm shell.

Authors	Year	Raw materials	Method	Application
Lua and Guo	2001	Oil palm stones	CO_2 activation	SO_2 removal
Hu and Srivinasan	2001	Coconut shell and palm shell	$ZnCl_2$ activation and CO_2 activation	Phenol, methylene blue
Guo and Lua	2003	Palm shell	H_3PO_4	Ammonia adsorption
Mozammel et al.	2002	Coconut shell	$ZnCl_2$activation	Iodine
Hu et al.	2001	Coconut shell and palm seed	$ZnCl_2$ activation	Phenol and dye
Daud and Ali	2004	Palm shell and coconut shell	Physical activation (N_2 gas)	Nitrogen adsorption

By now, a lot of research has been done on AC to improve the application of AC. One of the fastest growing areas is in environmental applications such as wastewater treatment. In the treatment of wastewater, it is used for purification, decolorization and the removal of toxic organics and heavy metal ions (Kim, et al., 2001). Recently, a researches have been focused more on removal of heavy metal ions such as copper (Kim et. al, 2001), zinc and chromium (Monser and Adhoum, 2002) and mercury (Budinova et. al, 2006). But only few researches have done on removal of cyanide pollutants by activated carbon. Adams (1994) studied the effect of copper in the adsorption of cyanide onto activated carbon. It was found that the removal capacity was highly improved by the presence of copper. Williams and Petersen (1997) reported that 56.5% of free cyanide (20 mg/l) could be removed using silver impregnated carbon compared with plain carbon (11 % CN removal). In column test, Monser and Adhoum (2002) observed that silver and nickel impregnated activated carbons could adsorb up to 26.5 and 15.4 mg CN per unit mass of adsorbent respectively compared with 7.1 mg CN/g for plain carbon.

Deveci et. al (2006) also reported that by using copper and silver impregnated activated carbon prepared from coconut shell could adsorb up to 22.4 and 29.9 mg/g CN respectively. Therefore, in this research the produce activated carbon will used to examine the potential application of local activated carbon produced on removal of cyanide pollutants.

1.2 The Importance of the Research

The world production of AC in 1990 was estimated to be 375,000 ton, excluding what was then Eastern Europe and also China (Mozammel et.al, 2002). In 2002, the demand for activated carbon reached 200,000ton per year in United States and the market will very probably be negatively affected by imports from the Asia-Pacific region. The demands of AC were increase over the year and market growth was estimated at 4.6% per year (Mozammel et. al, 2002). The strong market position held by AC relates to their unique properties and low cost compared with that of possible competitive inorganic adsorbents like zeolites.

AC is used primarily as an adsorbent to remove organic compounds and pollutant from liquid and gas streams. The market has been increasing constantly as a consequence of environmental issues, especially water and air purification. Furthermore, as more and more countries are becoming industrialized, the need for activated carbon to comply with environmental regulation will grow at faster rate. Liquid phase applications represent the largest outlet for AC. In these applications, AC is used in the purification of a variety of liquid streams, such as those used in water treatment and the processing of food, beverages and pharmaceuticals.

The growth of the activated carbon market in the last two decades in the most industrialized region will very probably continue in the near future as more developing areas of the world will realize the importance of controlling water and air pollution. This demand can be satisfied considering the large number of raw material available for the production of AC, the variety of activation processes described, and the available forms of AC. Thus, the continuous research has to be implementing to develop the high quality of AC for specific uses.

1.3 Objectives of the Research

The aim of this research is to produce activated carbon from the local agricultural waste which is coconut shell and palm kernel shell impregnated with two activation agent for a particular application. To achieve these, a study was carried out with the following objectives:

i. To evaluate various operating parameters such as activation temperature and activation time for the activated carbon produced from coconut shell and palm kernel shell.
ii. To study the effect of chemical activation on the development of pore structure on the activated carbon produced.
iii. To examine the characteristic of granular activated carbon produced (i.e elemental analysis, proximate analysis, adsorption capacity, surface functionality and pore size of AC produced).
iv. To evaluate the potential application of locally produced activated carbon in inorganic pollutants such as its performance in cyanide removal.

1.4 Scope of the research

Production of all these oils by the small scale or traditional producers is spread over various areas in the country, whilst the established industries engage mostly in production of palm oil. The supply of the palm shells is easier as many established industries dumped the shells as a waste after getting the kernels from the nuts. Coconut shell wastes, on the other hand, are spread over wider area in the country and collection ore effort than that of palm shells.

In this research, the production of activated carbon was carried out by using chemical activation method. In chemical activation, the carbonization and activation are accomplished in a single step by carrying out the thermal decomposition of the raw material impregnated with certain activating agents. Two activating agents were used, there are phosphoric acid and zinc chloride. Zinc chloride known as a Lewis acid is a strong dehydrating agent which could alter the structure of carbon to form the porous structure. While phosphoric acid, was also known as a strong acid acts as an acid catalyst to promote cleavage reactions (Rodriguez-Reinoso, 2002). By using these two chemical, the influences on the pore structure of AC produced can be compared.

After the impregnation step, the samples were carbonized in the horizontal furnace under inert atmosphere by using nitrogen gas (N_2) by varying the operating parameter such as carbonization temperature and carbonization time. The carbonization temperatures of this activation were varied between 300 to 500 ºC to analyze the effect of temperature on the yield and pores development of activated carbon.

This work also focuses on optimizing the activation time, instead to optimizing the activation temperature. The raw materials that have been activated will be carbonized under certain temperature with control time of 0.5, 1, 2, 3, 4 hours. After carbonization, the activated carbons produced were washed with water or hydrochloride acid several times until the residual activating agent on the surface of activated carbon completely removed.

This stage was important because during impregnation the activating agent will penetrated into raw material particles and occupied substantial volumes. Once they were extracted by intense washing, a large amount of microporosity was created.

In order to analyze the activated carbon produced, several standard analyses were employed to characterize the product that will meet the condition for commercialization. The characterization of the activated carbon produced were performed by using several analyses such as the elemental analysis, proximate analysis, pore size analysis, surface functional groups analysis and adsorption capacity.

CHAPTER TWO
LITERATURE REVIEW

2.1 ACTIVATED CARBON

2.1.1 Introduction

Activated carbons form a large and important class of porous solids, which have found a wide range of technological applications. As a consequence, the porous structures of these materials and their adsorption of gases, vapors, and liquids have been extensively studied. In this section the microstructural and porous properties of the principal classes of activated carbon are reviewed. It is outside the scope of this contribution to consider in detail the very many industrial applications and processes that employ activated carbon.

Activated carbons have been explained in different way of definition from several authors. In sec 2.1.2 the definition of activated carbons are reviewed from certain authors that give an overview about the activated carbons. On the other hand, some of the principal methods used to characterize the pore structure in activated carbons are outlined (Section 2.2). Furthermore, the pore structure is having been reviewed in section 2.3. In order to understand the porous structure of activated carbons it is first necessary to give an outline review of the carbonization processes that convert the organic precursors to the carbon product (Section 2.4). This provides a basis for understanding the relationship of the pore structure of activated carbons to the fine structure of the solid carbon materials. An appreciation of the fine structure of activated carbons leads to an account of the surface forces in pores that give rise to the powerful adsorptive properties of activated carbons.

The processing method involved two types of activation, physical and chemical activation (Sect. 2.5). The development of porosity in activated carbons by "physical" activation, i.e., by reaction of the carbon with oxidizing gases (steam. carbon dioxide. and air) is reviewed in Section 2.5.2. Chemical activation. i.e. by reaction *of* carbon precursors with reagents, such as phosphoric acid and zinc chloride is considered in Sect. 2.5.3. The review continues with a some applications of activated carbons (Sect. 2.6) and concludes with Sect. 2.7 that summarizes the salient points to emerge from the review.

2.1.2 Definition of Activated Carbon

Activated carbon (AC) as many known as a solid, porous, black carbonaceous material and tasteless. Marsh (1989) defined AC as a porous carbon material, usually chars, which have been subjected to reaction with gases during or after carbonization in order to increase porosity. AC is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface. While according to Norlia Baharun (1999) AC is an organic material that has an essentially graphitic structure. The main features common to all AC are; graphite like planes which show varying degrees of disorientation and the resulting spaces between these planes which constitute porosity, and the unit built of condensed aromatic rings are referred to as Basic Structure Units (BSU) (Benaddi,2000). Benaddi(2000) also stated that AC is predominantly an amorphous solid with a large internal surface area and pore volume. Cokes, chars and activated carbon are frequently termed amorphous carbon.

X-ray studies have shown that many so-called amorphous substances have crystalline characteristics, even though they may not show certain features, such as crystal angles and faces, usually associated with crystalline state. Although interpretation of the X-ray diffraction patterns is not free from ambiguities, there is general agreement that amorphous carbon consists of plates in which the carbon atoms are arranged in a hexagonal lattice, each atom, except those at the edge, being held by covalent linkages to three other carbon atoms. The crystallites are formed by two or more of these plates being stacked one above the other. Although these crystallites have some structural resemblance to a larger graphite crystal, differences other than size exist (Hassler,1974).

From all the definition, it can be summarized that AC is black, amorphous solid containing major portion of fixed carbon content and other materials such as ash, water vapor and volatile matters in smaller percentage. Beside that, AC also contain physical characteristic such as internal surface area and pore volume. The large surface area results in a high capacity for absorbing chemicals from gases or liquids. The adsorptive property stems from the extensive internal pore structure that develops during the activation process.

2.2 Characterization and Properties of Activated Carbon

Characterization for activated carbon (AC) is very important in order to classified AC for specific uses. Basically, AC characterized by physical properties and chemical properties. As Guo and Lua(2003) mentioned that the characteristics of activated carbon depends on the physical and chemical properties of the raw materials as well as activation method used.

Physical properties of AC, such as ash content and moisture content can affect the use of a granular AC and render them either suitable or unsuitable for specific applications. While the specific surface area of activated carbon and surface chemistry is classified as chemical properties. Furthermore, the porous structure of activated carbon also can be characterize by various techniques such as adsorption of gases(N_2, Ar, Kr, CO_2) or vapors (benzene, water), scanning electron microscopy(SEM) and transmission electron microscopy (TEM).

2.2.1 Moisture Content

Activated carbon is generally priced on a moisture free basis, although occasionally some moisture content is stipulated, e.g., 3, 8, 10%. Unless packaged in airtight containers, some activated carbons when stored under humid conditions will adsorb considerable moisture over a period of month. They may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, this moisture content does not affect the adsorptive power, but obviously it dilutes the carbon. Therefore, an additional weight of moist carbon is needed to provide the required dry weight.

2.2.2 Ash content

The ash content of a carbon is the residue that remains when the carbonaceous materials is burned off. As activated carbon contain inorganic constituents derived from the source materials and from activating agents added during manufacture, the total amount of inorganic constituents will vary from one grade of carbon to another. The inorganic constituents in a carbon are usually reported as being in the form in which they appear when the carbon is ashed.

Ash content can lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regeneration of used activated carbon. The inorganic material contained in activated carbon is measured as ash content, generally in the range between 2 and 10% (Yang, 2003).

To determine the content of ash, a weighed quantity (2 grams of powdered carbon, or 10 to 20 grams granular carbon) is placed in a porcelain crucible and heated in air in a muffle furnace until the carbon has been completely burned. The temperature should be below 600˚C to minimize volatilization of inorganic constituents, and also to leave the ash in a suitable condition for further examination.

2.2.3 Surface area

Generally, the larger the specific surface area of the adsorbent, the better its adsorption performance will be (Guo and Lua, 2003). The most widely used commercial active carbons have a specific surface area of the order of 600- 1200 m^2/g (Ng et.al, 2002). The pore volume limits the size of the molecules that can be adsorbed whilst the surface area limits the amount of material which can be adsorbed, assuming a suitable molecular size (Lartley, 1999). The adsorptive capacity of adsorbent is related to its internal surface area and pore volume.

The specific surface area (m^2/g) of porous carbon is most usually determined from gas adsorption measurement using the Brunauer-Emmett-Teller BET theory (Hu and Srinivasan, 1999). The most commonly employed method to characterize these structural aspects of the porosity is based on the interpretation of adsorption isotherm (e.g., N_2 at 77K). Nitrogen at its boiling point of 77K is the recommended adsorptive, although argon at 77K also used.

2.2.4 Surface Functional Group of Activated Carbon

The selectivity of activated carbons for adsorption is depended upon their surface chemistry, as well as their pore size distribution (Radovic,2001). Normally, the adsorptive surface of activated carbon is approximately neutral such as that polar and ionic species are less readily adsorbed than organic molecules.

For many applications it would be advantageous to be able to tailor the surface chemistry of activated carbon in order to improve their effectiveness. The chemical composition of the raw material influence the surface chemistry and offer a potentially lower cost method for adjusting the properties of activated carbons. For example, activated carbon fiber produced from nitrogen-rich isotropic pitches have been found to be very active for the catalytic conversion of SO_2 to sulfuric acid (Radovic,2001). Various surface functional groups containing oxygen, nitrogen and other heteroatoms have been identified on activated carbon. It because activated carbons have a large porosity and numerous disordered spaces, this makes heteroatom are readily combined on the surface during manufacturing processes (carbonization and activation). Heteroatoms are incorporated into the network and are also bound to the periphery of the planes. The heteroatoms bound to the surfaces assume the character of the functional groups typically found in aromatic compounds, and react in similar ways with many reagents. These surface groups play a key role in the surface chemistry of activated carbon (Yang ,2003).

There are numerous methods of determining surface functional groups and attempts have been made to study the surface groups by spectroscopic methods, for examples by infrared(IR). Figure 2.1 presents several IR- active functional groups that may be found at the edges of and within graphene layers after the oxidative treatment of active carbon.

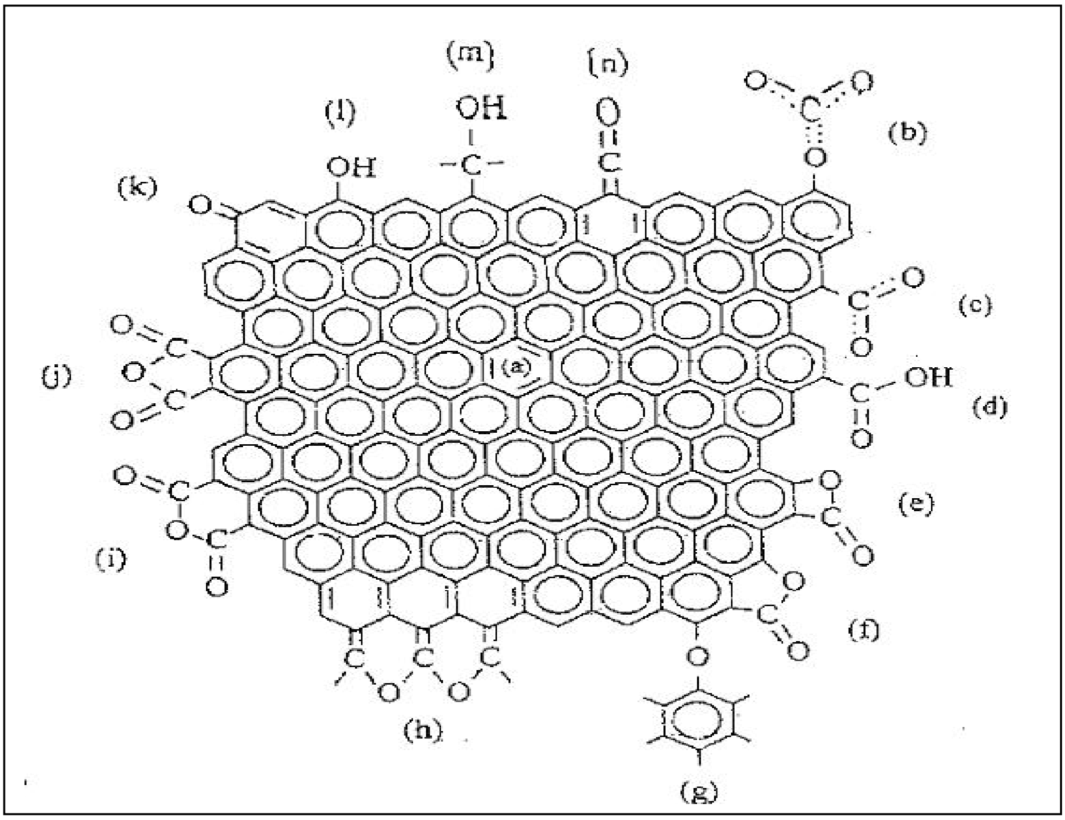


Figure 2.1 IR- active functionalities on carbon surfaces: (a) aromatic c=c stretching;(b) and (c) carboxyl-carbonates; (d) carboxylic acid; (e)lactone(4-membered ring);(f) lactone (5- membered ring); (g) ether brigde; (h) cyclic ether; (i) cyclic anhydride (5-membered ring); (j) cyclic anhydride (6-membered ring); (k) quinine; (l) phenol; (m) alcohol; and (n) ketene (Radovic, 2001).

2.3 Pore structure

The word pore comes from the Greek word, meaning a passage (Marsh, 1989). In this sense, a pore is a class of void which is connected to the external surface of a solid and will allow the passage of fluids into, out of, or through a material. Marsh's (1989) claim that, in the scientific literature on porous solids the terms 'open pore' and 'closed pore' are used, the former a pore which is not so connected. Examples of different pore types are shown schematically in Figure 2.2.

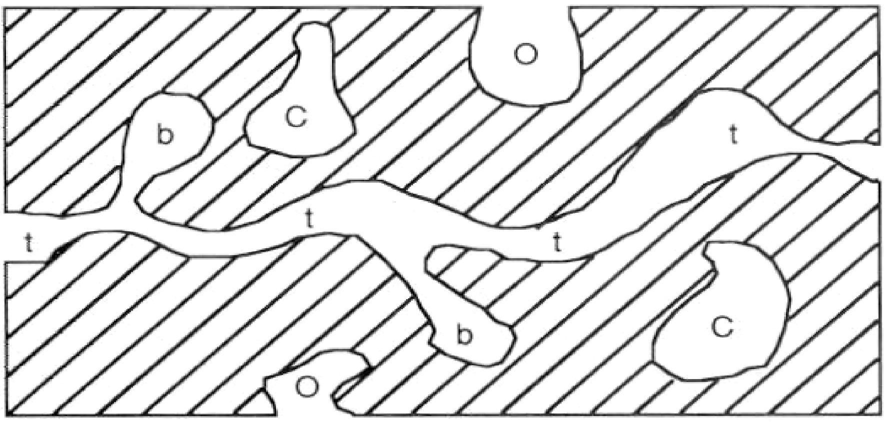


Figure 2.2 Different types of porosity in a porous solid (Marsh, 1989)
O-open pores; C- closed pores; t-transport pores; b-blind pores.

Transport pores are those pores in which a concentration gradient exists during steady state or time-independent fluid flow through the material. Blind pores are connected to transport pores by a single opening so that in them concentration gradients and hence fluid flow only occur during unsteady state or time independent flow.

Differences in pore sizes affect the capacity for molecules of different shapes and sizes, and this is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes (Guo and Lua, 2003):

i. Micropores- width less than 2nm
ii. Mesopores- width between 2 and 50nm
iii. Macropores- width greater than 50nm

The schematic of internal pores structure in activated carbon was shown in Figure 2.3 below.

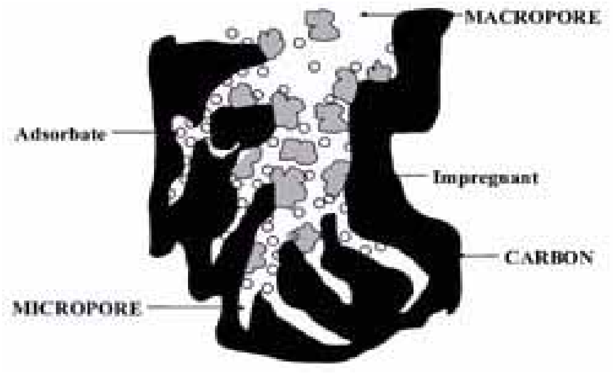


Figure 2.3 The schematic of internal pore structure in activated carbon (http://buildingprotection.rdecom.army.mil/images/af_carbon_pore.jpg)

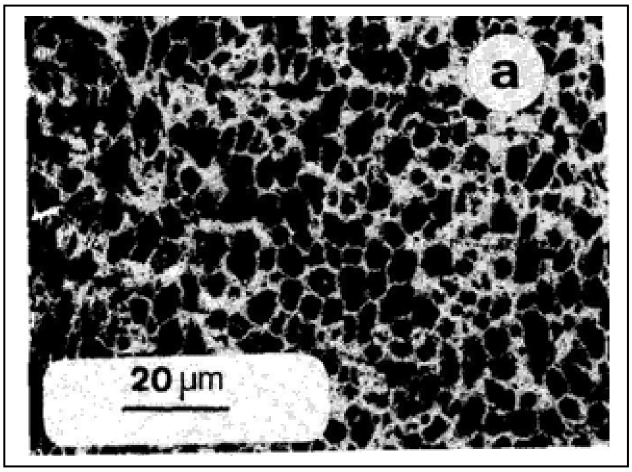


Figure 2.4 Cellular micropores in an almond shell carbon (Marsh, 1989).

The shapes of pores in activated carbon vary from slit- shaped cracks to spheroidal bubbles. Cracks may follow tortuous paths through the solid and may be connected to other pores to form an extensive and irregular network. The shapes of pores can have important effects on some properties of carbons and graphite, for example mechanical strength and kinetics reaction. An optical micrograph (Figure 2.4) of pores in an active carbon made from almond shells showed the section of the pores.

The micrograph is approximately elliptical with a mean equivalent circle pore diameter of about 15μm, so that they are large macropores. They are relics of the cellular structure of the precursor material. This is general characteristic of macropores in active carbon derived from lignocellulosic precursors. On the atomic scale, activated carbon have a very disordered carbon structure (Figure 2.5), as indicated in the high resolution electron micrograph of a cellulose carbon. Electron microscopical studies have led to models for the ultrastructure of activated carbons consisting of a twisted network of defective carbon layer planes cross-linked by aliphatic bridging groups.

Micropores are formed in the interlayer spacing with widths in the range 0.34-0.8nm. It is the micropores in activated carbon which have the greatest influence upon gas adsorption, while macropores and mesopores are important in transport of fluids to and from the micropores.

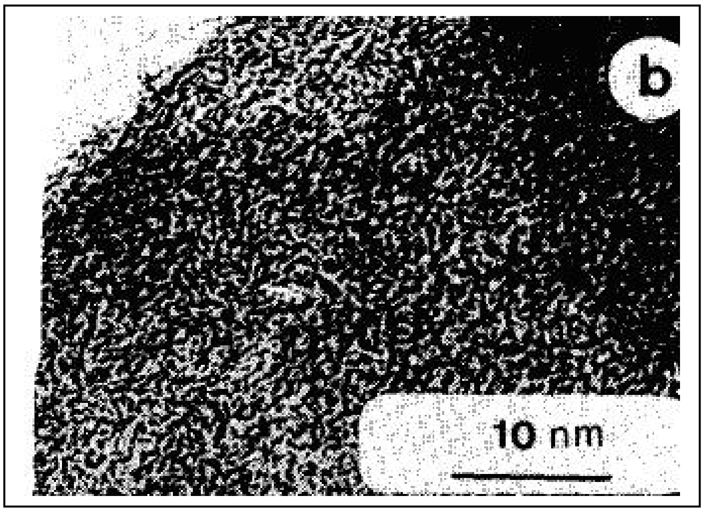
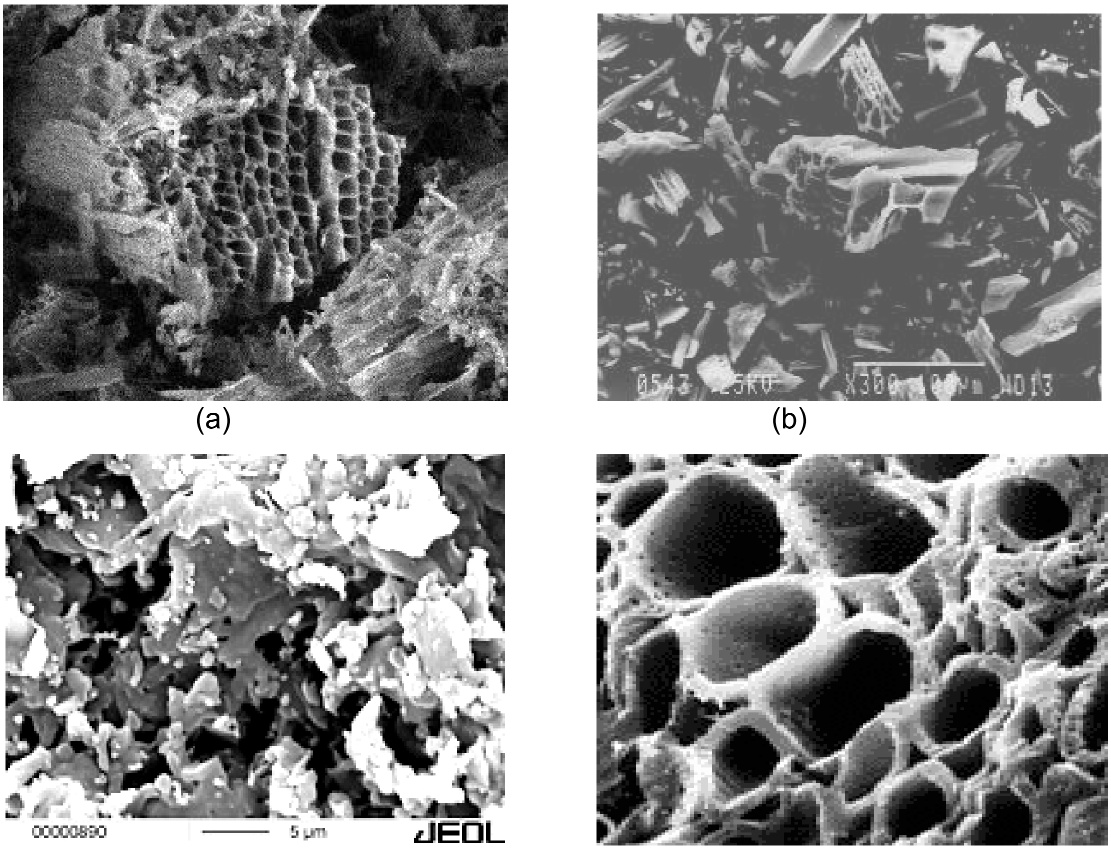


Figure 2.5 HREM of a cellulose carbon (Marsh, 1989)

Adsorption takes place in micropores and mesopores with macropores acting as transport channels. In adsorption from the gas phase, mainly microporous carbon is used whereas mesoporous carbon is applied in liquid phase processes (Benaddi et.al, 2000). Beside their significant contribution to adsorption, mesopores also serve as the main transport arteries for this adsorbate (Hu et al., 2001). The mesopores volume lies between the limits 0.1 to 0.5 cm^3 per gram and mesopores surface areas are in the range of 20 to 100 m^2 per gram (Hu et al., 2001). In carbon, mesopores can be formed by enlargement of micropores, for example by reaction with oxidizing gases as in activated carbon (Marsh, 1989).



(a) (b)

(c) (d)

Figure 2.6 SEM shows different shape of pores depending on types of raw materials.
(a) coal (http://www.air-purifier_home.com/images/2-ccoall.jpg),
(b) wood (http://www. Yahoo.com/images/pore carbon/activated carbon wood.jpg)
(c) husk (http://www. Yahoo.com/images/pore carbon/husk.jpg)
(d) coconut (http://www.lunor.ch/english/nbcfilters.html)

The distribution of pores in activated carbons can vary significant depending upon the raw material. Figure 2.6 shows the different shape of pore with different of raw material. The pore size distribution also affects the efficiency and selectivity of adsorption. A consideration of the dimensions of some pollutants shows that activated carbon can feasibly be used to remove many of the impurities occurring in water (Radovic, 2001). The small organic molecules with low solubility have sizes in the range 0.6 to 0.8 nm and can be adsorbed in micropores while large compounds such as color molecules and humid acids have dimensions around 1.5 to 3.0 nm that will favor their adsorption in mesopores. Figure 2.6 show the different of the pore distribution in activated carbon from different precursor materials.

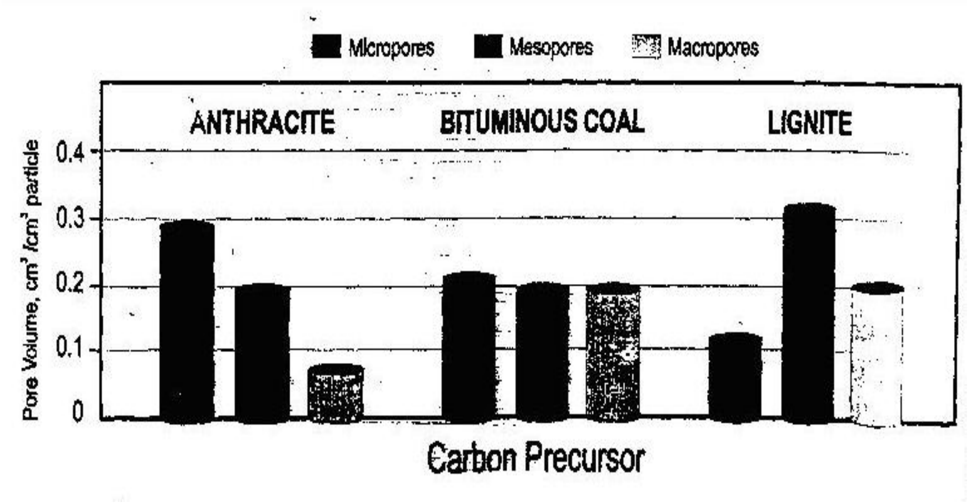


Figure 2.7 The pore distribution in activated carbon from different precursor materials (Radovic, 2001)

As in Figure 2.7, the activated carbon produced from different type precursor gave the different pore distribution. Activated carbon made from anthracite give a high proportion of micropores while activated carbons from bituminous coal give a broad pore size distribution while lignite produces mesoporous carbon.

A large part of the carbon surface is furnished by the walls of the pores, and such surface is accessible only to molecules that are small enough to enter. Table 2.1 showed the minimum pore diameter for adsorbate.

Table 2.1 Minimum pore diameter for adsorbate (Hassler,1974)

Adsorbate	**Minimum Pore, Diameter, Å**
Iodine	10
Potassium permanganate	10
Methylene Blue	15
Erythrosine Red	19
Molasses	28

2.4 The microstructure of activated carbon

Activated carbon, relatively known as amorphous carbon, show a very disordered microcrystalline structure in which graphitic microcrystals are randomly oriented (Gomez-Serrano et.al., 2005). The term "turbostratic" has been used to describe a-graphite like structure with random translation of layer planes along the a-axis and rotation of layer planes about the c-axis. The interlayer spacing in a turbostratic structure is 0.344 nm, which is larger than the spacing in a graphite single crystal^{-}, 0.3354 nm. Various microporous models have been proposed based on HRTEM studies (McEnaney,2002).

One of the examples of microporous structure for activated carbon is shown in figure 2.8. An essential feature of all of the models is a twisted network of carbon layer planes, crosslinked by an extended network of aliphatic carbon. The layer planes are defective, for example, they may contain vacancies and hetero-elements. The latter are bound to the edges of the layer planes as simple functional groups. e.g., -OH, C-O. -C--O -C-. There is a continuum of interlayer spaces ranging from the turbostratic value up to sizes that can form micropores.

Typically, in nongraphitizing carbons heated to -900 ˚C the interlayer spacing are separated by small stacks of two or three carbon layer planes. Thus, micropores are an inherent feature of the microstructure of activated carbon.

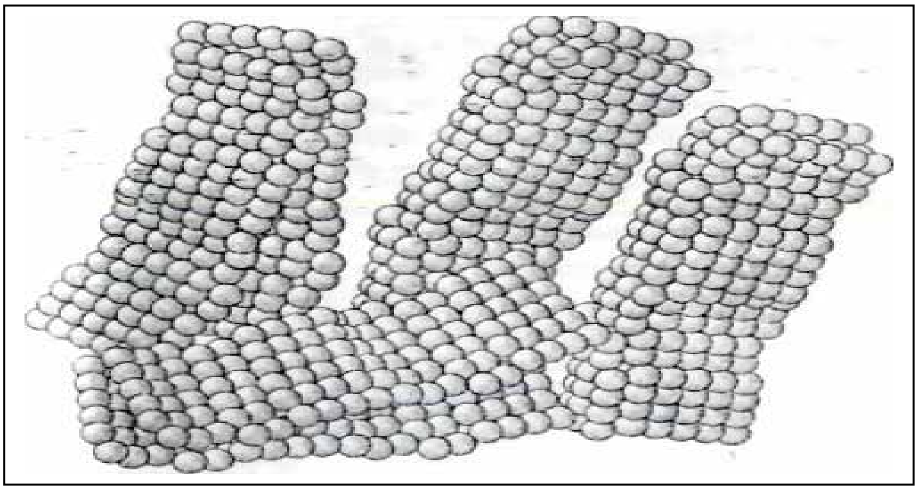


Figure 2.8 A model for the microstructure of a microporous carbon (McEnaney,2002)

Another feature of the microstructure is constrictions in the microporous network that control access to much of the micropore space (McEnaney,2002). Also. entrances to micropores may be blocked by functional groups attached to the edges of layer planes and by carbon deposits formed by thermal cracking of volatiles released during carbonization.

Thus, the micropores in activated carbons are incorporated into an aperture cavity network. Constrictions and blockages in the microporous network cause activated diffusion effects at low adsorption temperatures when the adsorptive has insufficient kinetic energy to penetrate the pore space completely (McEnaney,2002).

2.5 Processing of activated carbon

AC manufactured by the pyrolysis of carbonaceous materials of vegetable origin, such as wood, coal, peat, fruit stones, and shell or synthetic polymer followed by activation of the chars obtained from them (Manocha,2003). The pyrolysis of any carbonaceous material in absence of air involves decomposition of organic molecules, evolution of tarry and gaseous products, and finally in a solid porous carbon mass. An adsorbent with highly developed porosity and correspondingly large surface area is obtained only by activating the carbonized material either by physical or chemical activation. The processing of AC basically involves selection of parameters that effecting the activated carbon production, carbonization process and types of activation.

2.5.1 Factors Affecting Activated Carbon Production

(1) Raw material

Most organic materials rich in carbon that do not fuse upon carbonization can be used as raw material for the manufacture of AC (Rodriguez-Reinoso,2002). The selection of raw material for preparation of porous carbon, several factors are taken into consideration.

The factors are:

i. High carbon content
ii. Low in inorganic content (i.e low ash)
iii. High density and sufficient volatile content
iv. The stability of supply in the countries
v. Potential extent of activation
vi. Inexpensive material

vii. Low degradation upon storage

Lignocellulosic materials constitute the more commonly used precursor and account for around 45% of the total raw materials used for the manufacture of activated carbon. Low content in organic materials is important to produce AC with low ash content, but relatively high volatile content is also needed for the control of the manufacturing process.

Raw material such as coconut shell and fruit stones are very popular for many types of AC, because their relatively high density, hardness and volatile content are ideal for manufacture of hard granular AC. Coconut shells, together with peach and olive stones are used commercially for the production of microporous activated carbons, useful for a very wide range of applications. Further details about the characteristic of raw materials used for making activated carbon are listed in Table 2.2.

Table 2.2 Characteristics of various conventional raw materials used for making AC (Manocha, 2003)

Raw materials	Carbon (%)	Volatile (%)	Density (Kg/m^3)	Ash (%)	Texture of AC
Softwood	40-45	55-60	0.4-0.5	0.3-1.1	Soft, large pore volume
Hardwood	40-42	55-60	0.55-0.8	0.3-1.2	Soft, large pore volume
Lignin	35-40	58-60	0.3-0.4	-	Soft, large pore volume
Nut shells	40-45	55-60	1.4	0.5-0.6	Hard, large multi pore volume
Lignite	55-70	25-40	1.0-1.35	5-6	Hard small pore volume
Soft coal	65-80	25-30	1.25-1.50	2.12	Medium hard, medium micropore volume
Petroleum coke	70-85	15-20	1.35	0.5-0.7	Medium hard,medium micropore volume
Semi hard coal	70-75	1-15	1.45	5-15	Hard large pore volume
Hard coal	85-95	5-10	1.5-2.0	2.15	Hard large volume

(2) Temperature

Temperature, particularly the final activation temperature, affects the characteristic of the activated carbon produced. Generally, for commercial activated carbon usually conducted at temperature above 800˚C in a mixture of steam and CO_2 (San Miguel, et al.,2003). Recently, the researches have been working out on optimizing the final activation temperature to economize the cost of production and time. As reported by several authors, activation temperature significantly affects the production yield of activated carbon and also the surface area of activated carbon. The temperature used as low as 200˚C(Haimour and Emeish,2005) and up high to 1100˚C (San Miguel, et al.,2003).

The optimum temperatures have been reported to be between 400˚C to 500˚C by most the earlier researchers irrespective of the time of activation and impregnation ratio for different raw material (Srinivasakannan and Zailani, 2003). The increasing of activation temperature reduces the yield of the activated carbon continuously. According to Guo and Lua(2003), this is expected since an increasing amount of volatiles is released at increasing temperature from 500˚C to 900˚C. The decreasing trend in yield is paralleled by the increasing activation temperature due to the activation reaction. These phenomena are also manifested in the decreasing volatile content and increasing fixed carbon for increasing activation temperature. Previously, Haimour and Emeish(2005) suggested that the percentage of volatile matter decreased with an increased of carbonization temperature and the variation of this parameter was maximum between 200˚C and 800˚C due to rapid carbonization occurring in this region. It is also unsuitable to prepare activated carbon when carbonization temperature was more than 800˚C since the successive decreased in volatile matter is minimal above this range.

This was accompanied with an increased of fixed carbon and ash content which may be attributed to the removal of volatile matter in the material during carbonization process. Thus, leaving behind the more stable carbon and ash-forming minerals (Haimour and Emeish, 2005). Another notable feature that showed the effect of activation temperature on the activated carbon properties is the BET surface area. As the activation temperature increased, the BET surface area also increased (Haimour and Emeish, 2005). This may be attributed to the development of new pores as a result of volatile matter released and the widening of existing ones as the activation temperature become higher.

(3) Activation time

Besides activation temperature, the activation time also affects the carbonization process and properties of activated carbon. From previous study, the activation times normally used were from 1 hour to 3 hour for palm shell and coconut shell (Srinivasakannan and Zailani, 2003). As the time increased, the percentage of yield decreased gradually and the BET surface area also increased. This result is possibly due to the volatilization of organic materials from raw material, which results in formation of activated carbon. The extent of decrease in product yield is observed to be reducing when excessive activation occurs (Kim et al., 2001).

2.5.2 Carbonization

During carbonization, most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting materials, and the free atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphite crystallites (Manocha, 2003). The original organic substance may be split into fragments which regroup to form the thermo-stable aromatic structure existing in the hexagon.